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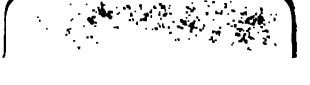
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PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

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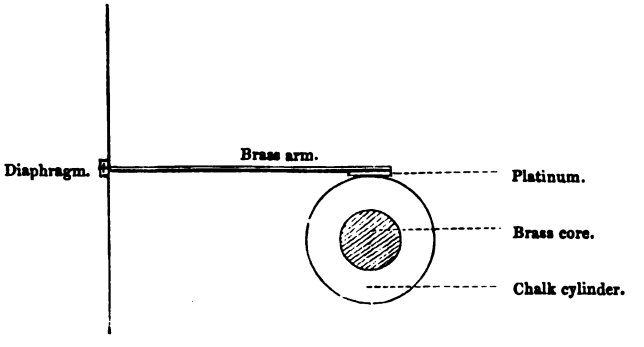
AUGUST 1880.

I. *The Influence of Friction upon the Generation of a Voltaic Current.* *By* SHELFORD BIDWELL, *M.A.**

IN 'Nature' of March 4th Prof. Barrett calls attention to the fact (which I believe had been observed before) that the electro-motograph, or receiving-instrument of Edison's loud-speaking telephone, is capable of generating an electric current. He considers that we have here a new source of electricity, the current generated being due to the motion of a chalk cylinder under a metallic surface. His chalk, he adds in a note, had been impregnated some months before with a solution of phosphate of soda, but was, when used, practically dry.

The construction of the motograph is essentially as follows:—One end of an arm of brass is joined to the diaphragm of the instrument; the other end, which is faced with platinum, is pressed by a spring against the upper surface of a horizontal chalk cylinder. This cylinder is mounted on a thick brass core or spindle, and can be made to rotate and rub against the platinum on the arm by turning a winch-handle. The cylinder is impregnated with certain chemical substances, of which I believe caustic potash is always one, though it is not mentioned by Prof. Barrett.

* Read March 13, 1880.



It will be seen that there are here two metals, brass and platinum, connected by a medium containing caustic potash; and the arrangement looks so much like a voltaic couple that I was not surprised, on connecting the brass and platinum to a galvanometer, to find a small + current flowing from the platinum-faced arm. The cylinder was not rotated, and had not been moistened for some months. On turning the handle the galvanometer at once indicated a much stronger + current passing from the platinum. The effect of the friction was to greatly increase the strength of the current.

I then faced the brass arm with zinc instead of platinum. On connecting the instrument to the galvanometer a small deflection was again observed; but this time the + current flowed, as I expected, not from the zinc-faced arm, but from the brass core of the cylinder. The substitution of the zinc for the platinum had the effect of reversing the current, brass being positive to platinum and negative to zinc. In this case too, rotation of the cylinder largely increased the current.

I now laid aside the motograph, and connected to the two wires of the galvanometer a sheet of brass and a sheet of platinum. Between these metallic plates I placed a thin slice of dry chalk; the galvanometer indicated nothing. I rubbed the metals successively against the chalk; still the galvanometer remained motionless. For the pure chalk I substituted a chalk plate which had been soaked in a saturated solution of phosphate of soda and thoroughly dried; again there was no result. Neither was there when I used dry blotting-paper which had been saturated with phosphate of soda. But with

a piece of blotting-paper which had been saturated with a solution of caustic potash and made as dry as possible, the results were just the same as with the electro-motograph: brass and platinum gave a + current from the platinum; brass and zinc gave a + current from the brass; and in both cases the current was much increased by rubbing.

This experiment was repeated with the following pairs of metals—brass and platinum, zinc and lead, zinc and copper, lead and copper, tin and copper, zinc and tin—covering one of every pair of metals successively with a wet cloth and rubbing the one so covered with the other. In every case the friction seemed to considerably increase the current which was generated on mere contact. If, for instance, a piece of lead is covered with a wet cloth and a piece of copper is pressed upon it, a + current will of course flow from the copper. On rubbing, this current is very greatly increased. If the copper be the metal covered, and the lead rubbed against it, the current from the copper will again be greatly increased, but apparently not quite so much so as in the former case. And I believe that this difference in the effect produced according to the metal covered, occurs in the case of all the other pairs of metals which I tried. In some cases it is very notable; in others it is small, and extremely difficult to detect without a machine for producing uniform friction. But, as far as I can judge, the effect on the current is always greatest when the positive element is covered and the negative element exposed to friction.

It seems, therefore, that Prof. Barrett's experiment is only an illustration of the effect of friction on one of the elements of a voltaic couple in increasing the current. This effect is, however, so very remarkable that I was induced to make further experiments.

The most curious result at which I arrived is this:—Take two plates of the same metal, cut from the same sheet, and connect them with a galvanometer; cover one of them with a wet cloth and bring the other down upon it. If the two pieces of metal are in the same physical condition there will be no material deflection of the galvanometer. Now rub the covered metal with the bare metal. As long as the rubbing continues, the galvanometer indicates a current of electricity,

which ceases as soon as the rubbing is stopped. And this current invariably flows from the plate which is covered by the wet cloth.

I have made the experiment with plates of tin, lead, copper, brass, and zinc, with the same result in every case.

I do not suggest an explanation of the above-mentioned phenomena. When the two plates of a single metal are used, it appears that friction renders the one rubbed relatively electro-positive. But in the case of two metals, friction seems generally to have a greater effect upon the negative than the positive element, and it makes the negative element not more positive but more negative. Any possible explanation that occurs to me of the one case is inconsistent with the other.

Certain speculations led me to try the effect of passing a battery-current through a pair of metallic plates, separated by a piece of wet rag or paper, while they were being rubbed together; and I found that when the current passed from the covered to the uncovered plate, a remarkable diminution in the friction occurred. A current in the opposite direction produced no such result. I exhibit a little apparatus for rendering this effect visible to a large audience.

This experiment seems to show conclusively that the generally received theory of electrolytic action is sufficient to explain the phenomena presented by the electro-motograph; for it is difficult to conceive any other possible effect of the current than the liberation of hydrogen on the surface of the plate which is connected with the negative pole of the battery, the layer of hydrogen having the effect of diminishing the friction.

Riverstone Lodge, Wandsworth, S.W.

II. *On some Effects of Vibratory Motion in Fluids; on the Attraction due to the Flow of Liquids from an Expanded Orifice; and Laboratory Notes.* *By* R. H. RIDOUT.

On some Effects of Vibratory Motion in Fluids.

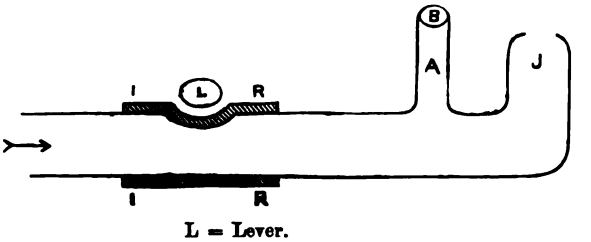
ON causing a stream of coal-gas to bubble through a liquid contained in a flask, it may by careful adjustment be made to issue from a suitable jet in an oscillatory manner, in the plane which would contain a sensitive flame issuing from

the same jet. Thus a flame may be sensitive when the disturbance is imparted from within.

An analogous experiment with water was attempted as follows:—An electromagnetic engine was made to oscillate a lever, pressing against an india-rubber tube, conveying water from a height of 14 feet to a partially closed tube, such as would emit a sensitive flame under a moderate pressure. The water issued in a pulsatory manner, but showed no new form.

On comparing the two experiments, it will be seen that the bubble of gas, in passing through the liquid, is gradually increasing in volume, and when it reaches the surface, probably expands to a size it could not permanently retain. Such is not possible with water; for though its elasticity is greater than that of air, the range through which it acts (which may be called its amplitution) is much less. To provide for this amplitution, an air-chamber was introduced between the lever and the jet (fig. 1). The water then issued in exactly the

Fig. 1 (section).



L = Lever.
I R = India-rubber tube.
A = Air-chamber.
B = Air-bubble.
J = Jet.

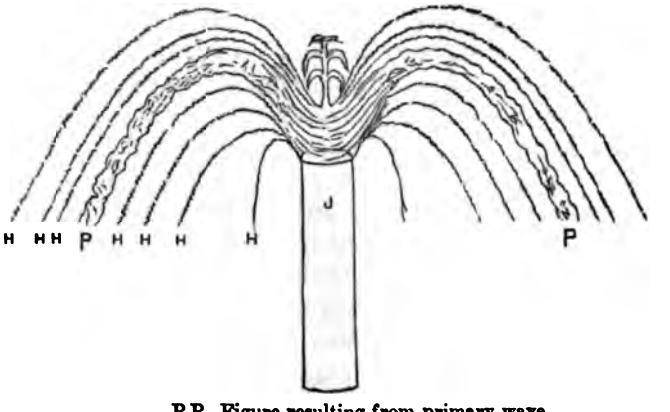
same manner as an excited sensitive flame, breaking into two streams lying in *one* plane. The motion of the lever upon the flowing water produces in the latter a sinuous wave; and as the troughs and crests reach opposite sides of the jet, they take alternatively opposite directions, forming two complete streams with about 400 vibrations per second. On substituting a straight tube for the jet, figures of great beauty were obtained.

Fig. 2 shows a simple wave free from harmonics. The phase of the wave relatively to the lever's motion is so strongly marked, that it is not destroyed by passing through tortuous

tubes 2 feet long. When the lever presses the tube at any but a right angle, the figures are more complex and show a tendency to rotation.

A wave with harmonics produces minor streams (fig. 3) in

Figs. 2 and 3.



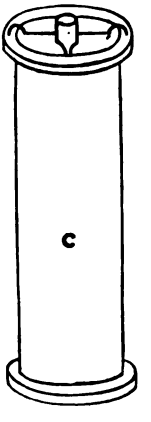
P P. Figure resulting from primary wave.
H H &c. Harmonics. J. Straight tube.

addition to the primary one. I have shown in 'Nature' (Oct. 3, 1878) that a flame is capable of producing harmonics of its primary note; and this makes the analogy complete between gaseous and liquid columns, in their behaviour to sensible vibratory motion.

The experiment analogous to the ordinary sensitive flame was attempted by immersing a sensitive jet in a vessel of water and passing a coloured liquid. The jet always "roared" when a higher pressure than $\frac{1}{2}$ in. water was used. Near the critical point I could not produce any marked effect by applying to the water a 4-inch tuning-fork. Possibly larger apparatus would give better results. While working with this, I was struck with the great depth to which a stream of the liquid will descend under a very small pressure from a non-sensitive jet, made by contracting a $\frac{5}{8}$-inch test-tube to about $\frac{1}{16}$ inch, and cutting off some distance below the contraction. When a liquid flows through this with a fall of $\frac{1}{4}$ inch into a tall cylinder of the same liquid, it continues in an unbroken line for 8 inches or more, having the diameter of the smallest part. Recalling a deduction of Froude's, that a liquid flowing through

a tortuous tube without friction has no tendency to straighten it, I mounted the jet on pivots, and, by giving it an oscillatory motion, found that the stream travelled the liquid as a perfect wave, showing the deduction to be experimentally true. This apparatus (fig. 4), if mounted on the board carrying the vibrating lever and water-jet, gives a graphic representation of the wave which is producing the figures (figs. 2 and 3), and shows the presence or absence of harmonics.

Fig. 4.

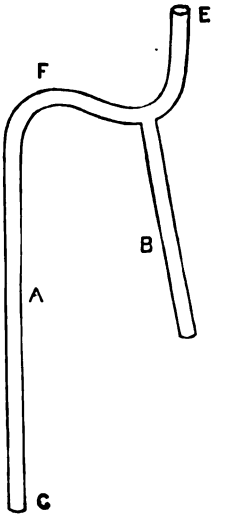


By using in the glass cylinder a weak solution of oxalic and sulphuric acids, and supplying the jets with a solution of sulphuric acid and permanganate of potash of exactly the same density, the waves are extinguished after a few seconds, while the liquid remains quite clear.

It will be seen that the streams (figs. 2 and 3) soon break into beads. On receiving these in water, they manifest the spheroidal state in a high degree.

When the bubble of air in the air-chamber (fig. 1) is above a certain size it splits into several lesser ones; and these on entering the current have a less velocity than the water towards the jet. Fig. 5 shows how this effect may be magnified. In a glass tube of ¼-inch bore, the limb A is about 1 foot long and closed at C. An india-rubber tube is attached at E, and bent back at a small angle in order to vibrate, as in the Bunsen pump. B is the waste-pipe. A bubble of air, the size of a rape-seed, is placed in the bend at F, A being full of water. When the current of water through E causes the whole to vibrate, the air-bubble detaches itself from the tube, takes the shape of a string of four or five beads, and sinks through the water to C, where it remains as long as the vibration continues. Attempts were made to substitute sphericles of glass,

Fig. 5.



shellac, wax, &c., each made a little lighter than water, but without success. If the result were due to the passage of vibration being more rapid in water than air, then globules of mercury, bromine, and bisulphide of carbon, all of which have a greater velocity for sound than water, should either float or show some tendency to do so. A great number of experiments, under varying conditions, failed to show that they were in any way affected.

As an air-bubble sinks as rapidly as a grain of sand would do, I tried hydrogen in place of air, and mercury in place of water in the tube A. When the hydrogen reaches the mercury it rests a little, and then suddenly sinks with the same apparent velocity as the air in water.

If in these experiments the bubble is large it does not descend; and this points to the close analogy with the experiments of Guthrie (Proc. Roy. Soc. 1870, pp. 35–41), who found that the vibration of a solid body caused the "approach" of a piece of cardboard from a considerable distance. We might say, conventionally, that the attraction was less between the air and the sounding body than the cardboard and the latter. Now in the tube A, C being a node, any particle near C is relatively at rest to one nearer E, and the attraction between them is greater than either for the bubble. Hence the particle at C tends to move towards E, or, what is the same thing, the bubble moves to C. When the bubble is large it is still repelled, but it leaves no way for the approach of the attracted water. A great number of small bubbles may be successively sunk till a large one results at C, showing that the conditions of the experiment only proscribe the motion of the large one. By inverting fig. 5 it may be used to produce the water-figures; but they can seldom be obtained free from harmonics by such means.

On the Attraction due to the Flow of Liquids from an Expanded Orifice.

M. Lacoutre has shown in *Les Mondes* for May 10, 1866, that when a liquid flows perpendicularly from a cylindrical tube upon a flat disk, its motion is arrested till the disk is brought to within half a diameter of the tube (but varying with pressure), when the outflow is greater than if the disk be

entirely removed. I find that if the tube terminate in a similar disk, attraction ensues at the position of greatest outflow.

A glass filter funnel containing a light cone with a weight dependent from its apex, or a tube terminating in a hemispherical cup with a light ball, have more stability than the disks, and answer equally well. In all cases the apparatus may be immersed in liquid and the attraction continued. The explanation usually accepted of the corresponding pneumatic experiment of M. Clément Desormes, is based on the assumption that the velocity of the fluid gradually decreases as it approaches the edges of the disks. To determine how far this was generally true, I took an outer cone A of 4 inches diameter at base with angle of 60° at apex, and an inner cone B upon same base with angle of 120°. For the velocity of the liquid to diminish between the apex of B and base of A, the cones must be separated nearly $\frac{1}{4}$ inch. Using water at varying pressure, in no case did attraction take place at more than $\frac{1}{10}$ in., where the velocity must *increase* towards the outlet. I find also that the presence of the attracted cone, ball, &c. diminishes the pressure in the supply-pipe, as shown by a water-guage attached to the latter. Hence the presence of the cone &c. facilitates the efflux.

Laboratory Notes.

Apparatus for showing Electrolysis of Water.

A glass bolthead of 30 or 40 oz. capacity is stopped with an india-rubber cork carrying two glass tubes, which contain hermetically sealed platinum wires, projecting an inch at the inner end and terminating in binding-screws at the other. The vessel is filled one fifth full of acidulated water, boiled, and the stopper inserted to cause a vacuum when cold. On connecting with two "Grove" cells, the bubbles of gas so expand as to make the whole liquid appear to boil. With either a single "Grove," "Bunsen," "bichromate," or "Leclanché" cell continuous decomposition may be obtained. When sufficient gas has collected to impair the vacuum it may be restored by boiling.

Experiment showing Cohesion in Liquids.

A shallow tray $6'' \times 2''$, open at one end and lipped, is supported on three levelling-screws, the lipped end being *slightly*

higher than the other. A quantity of mercury placed in the tray falls to the lower end; but if now a little more be added to make it flow over the lip, the cohesion is such as to enable the descending stream to drag the remainder up the inclined plane. Water gives similar results; but, from the difficulty of getting a surface which will long remain unwetted, the results are not so satisfactory.

Production of a Musical Note in a Continuous Tube.

In most wind instruments the sound results either from the movement of a solid body, or the air has the choice of two directions, which it alternately takes. I find, however, that it is possible to produce a good note from a tube $\frac{1}{4}$ to $\frac{5}{8}$ inch in diameter, and from 6 inches to a foot long, and having a part of it contracted smoothly and evenly to about a fourth of its diameter, by blowing through it. If the tube be bent upon itself at the point of contraction, the sounds are more readily obtained, though not of greater intensity.

Apparatus for showing Absorption of Heat on Liquefaction of Solids.

In a differential air-thermometer, the usual flasks are replaced by others which have had their bottoms softened, and then introverted to form a cup or basin. In this latter water is placed, and the solid then added. Any change in the liquid's temperature is at once communicated to the air-space round the cup.

Experiment showing the Expansion of Glass by Heat, and its low Conducting-power.

A glass tube of $\frac{1}{8}$-inch bore and 18 inches long is bent into the form of a violet-leaf—its free ends forming the apex, and leaving an interval in which a coin may be held by the elasticity of the glass. When heat is applied to the convex side of the middle bend, the limbs open and the coin falls.

III. *Preliminary Notes on* Mr. Hall's *Recent Discovery.*

By H. A. ROWLAND*.

THE recent discovery by Mr. Hall† of a new action of magnetism on electric currents opens a wide field for the

* From the American Journal of Mathematics.

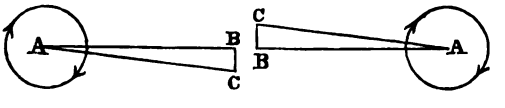
† Phil. Mag. [5] vol. ix. p. 225.

mathematician, seeing that we must now regard most of the equations which we have hitherto used in electromagnetism as only approximate, and as applying only to some ideal substance which may or may not exist in nature, but which certainly does not include the ordinary metals. But as the effect is very small, probably it will always be treated as a correction to the ordinary equations.

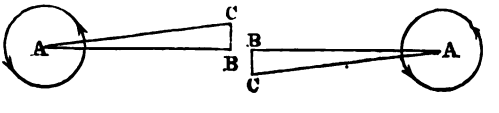
The facts of the case seem to be as follows, as nearly as they have yet been determined:—Whenever a substance transmitting an electric current is placed in a magnetic field, besides the ordinary electromotive force in the medium, we now have another acting at right angles to the current and to the magnetic lines of force. Whether there may not be also an electromotive force in the direction of the current has not yet been determined with accuracy; but it has been proved, within the limits of accuracy of the experiment, that no electromotive force exists in the direction of the lines of magnetic force. This electromotive force in a given medium is proportional to the strength of the current and to the magnetic intensity, and is reversed when either the primary current or the magnetism is reversed. It has also been lately found that the direction is different in iron from what it is in gold or silver.

To analyze the phenomenon in gold, let us suppose that the line A B represents the original current at the point A, and that B C is the new effect. The magnetic pole is supposed to be either above or below the paper, as the case may be. The line A C will represent the final resultant electromotive force at the point A. The circle with arrow represents the direction in which the current is rotated by the magnetism.

North Pole above.



North Pole below.



It is seen that all these effects are such as would happen were the electric current to be rotated in a fixed direction with respect to the lines of magnetic force, and to an amount depending only on the magnetic force and not on the current. This fact seems to point immediately to that other very important case of rotation, namely the rotation of the plane of polarization of light. For, by Maxwell's theory, light is an electrical phenomenon, and consists of waves of electrical displacement, the currents of displacement being at right angles to the direction of propagation of the light. If the action we are now considering takes place in dielectrics, which point Mr. Hall is now investigating, the rotation of the plane of polarization of light is explained.

I give the following very imperfect theory at this stage of the paper, hoping to finally give a more perfect one either in this paper or a later one.

Let $\mathfrak{H}$ be the intensity of the magnetic field, and let E be the original electromotive force at any point, and let ς be a constant for the given medium. Then the new electromotive force E′ will be

$$E' = \varsigma \mathfrak{H} E,$$

and the final electromotive force will be rotated through an angle which will be very nearly equal to $\varsigma\mathfrak{H}$. As the wave progresses through the medium, each time it (the electromotive force) is reversed it will be rotated through this angle; so that the total rotation will be this quantity multiplied by the number of waves. If λ is the wave-length in air, and i is the index of refraction, and c is the length of medium, then the number of waves will be $\frac{ci}{\lambda}$, and the total rotation

$$\theta = cc\mathfrak{H}\frac{i}{\lambda}.$$

The direction of rotation is the same in diamagnetic and ferromagnetic bodies as we find by experiment, being different in the two; for it is well known that the rotation of the plane of polarization is opposite in the two media, and Mr. Hall now finds *his* effect to be opposite in the two media. This result I anticipated from this theory of the magnetic rotation of light.

But the formula makes the rotation inversely proportional

to the wave-length, whereas we find it more nearly as the square or cube. This I consider to be a defect due to the imperfect theory; and it would possibly disappear from the complete dynamical theory. But the formula at least makes the rotation increase as the wave-length decreases, which is according to experiment. Should an exact formula be finally obtained, it seems to me that it would constitute a very important link in the proof of Maxwell's theory of light, and, together with a very exact measure of the ratio of the electromagnetic to the electrostatic units of electricity which we made here last year, will raise the theory almost to a demonstrated fact. The determination of the ratio will be published shortly; but I may say here that the final result will not vary much, when all the corrections have been applied, from 299,700,000 metres per second; and this is almost exactly the velocity of light. We cannot but lament that the great author of this modern theory of light is not now here to work up this new confirmation of his theory, and that it is left for so much weaker hands.

But before we can say definitely that this action explains the rotation of the plane of polarization of light, the action must be extended to dielectrics, and it must be proved that the lines of electrostatic action are rotated around the lines of force as well as the electric currents. Mr. Hall is about to try an experiment of this nature.

I am now writing the full mathematical theory of the new action, and hope to there consider the full consequences of the new discovery.

Addition.—I have now worked out the complete theory of the rotation of the plane of polarization of light, on the assumption that the displacement currents are rotated as well as the conducted currents. The result is very satisfactory, and makes the rotation proportional to $\frac{i^5}{\lambda^2}$, which agrees very perfectly with observation. The amount of rotation calculated for gold is also very nearly what is found in some of the substances which rotate the light the least. Hence it seems to me that we have very strong ground for supposing the two phenomena to be the same.

III. *Complete Theory of the Bifilar Magnetometer and new Methods for the Determination of the Absolute Horizontal Intensity of the Earth's Magnetism, as well as of the Temperature and Induction-coefficients of Magnets.* *By* H. WILD.

THE above is the title of a communication made to the Imperial Academy of Sciences of St. Petersburg on the 15th (27th) January, 1880 (*Bull. Acad. Impér. Sci. St. Pétersburg, Mélanges Phys. et Chim.* xi.), as an abstract of a more detailed paper to be shortly laid before the Academy.

The starting-point of the paper is the observation that the indications of the bifilar magnetometer, even when all causes of disturbance are excluded, differ from the results of direct measures of horizontal intensity to a far greater extent than can be accounted for by errors of observation. The author traces the cause of these discrepancies in the twisting of the suspending fibres, of which no account is taken in the ordinary theory of the bifilar magnetometer, according to which the moment of the directive couple of the suspension is ascribed simply to the weight of the magnet and its stirrup. The effect which this cause is capable of producing may either be calculated from the dimensions and coefficient of torsion-elasticity of the fibres, or it may be determined experimentally upon the bifilar instrument itself by observing the period of vibration before and after a known change has been made in the moment of inertia. Concordant determinations by both methods indicated that in the case of a bifilar suspended by brass wires 4 metres long, the couple due to torsion amounted to 1 per cent. of that due to the suspended weight. In the bifilar magnetometer of the St.-Petersburg magnetograph, which was suspended by steel wires only 0·3 metre long, the effect of torsion was as much as about 7 per cent. of the gravitation-couple. On the other hand, it amounted to only 0·3 per cent. in a bifilar of the Pawlowsk Observatory, this instrument having cocoon fibres 1·2 metre long. From the consideration of the conditions which determine the magnitude of the torsion and gravitation-couples respectively, Prof. Wild concludes that it is not probable that the proportion between them can be reduced much below that which exists in the last-mentioned instrument, namely 0·3 per cent., and hence

that the correction for torsion cannot be of negligible amount in accurate observations.

When this correction is applied, as well as that for induction, the author finds that the differences between the results of calculation and experiment disappear, and that very nearly identical values of the characteristic magnitude of the bifilar magnetometer, namely the so-called "torsion-angle" z, are obtained by both methods. The reader may be reminded that this angle z is the angle which a vertical plane passing through the upper ends of the suspending fibres makes with a vertical plane through their lower ends when the magnet is perpendicular to the magnetic meridian. If D be the moment of the directive couple due to the suspension, H the earth's horizontal intensity, and M the moment of the magnet, the angle z is defined by the equation

$$D \sin z = HM.$$

Its magnitude may be found by direct experiment; or it may be calculated from the periods of vibration of the magnet observed when its position of equilibrium is in the magnetic meridian and its north-seeking pole is towards magnetic north and its south-seeking towards magnetic south respectively. If t_1 and t_2 are the periods in the two cases,

$$\sin z = \frac{t_2^2 - t_1^2}{t_2^2 + t_1^2}.$$

The author observes, in the next place, that the direct determination of z, together with the observation of the periods t_1, t_2, t_3 (the last being the period of vibration when the position of equilibrium of the magnet is perpendicular to the meridian), affords an excellent method for determining separately the two induction-coefficients of the magnet, namely the coefficient of increase and that of decrease of the magnetic moment. The advantages of this method are chiefly that it does not depend upon the mutual action of two magnets, which can be only approximately calculated, and that it requires the use of only one instrument. He also remarks that these advantages apply also to the method indicated by him in a previous publication for the determination of the temperature-coefficients of magnets, and that he has assured himself by actual trial of the precision of this method.

The remainder of the paper is devoted to the description of a process for determining in absolute measure the earth's horizontal magnetic intensity by means of the bifilar magnetometer, and to the statement of the formulæ required for the complete reduction of the results so as to take account of all corrections. The principles involved in this process may be thus indicated:—It is divisible, like Gauss's process, into a method for determining (*a*) the product of the horizontal intensity H into the moment M of a particular magnet, and (*b*) the ratio of the same two quantities. To determine the *product*, the magnet is suspended in the bifilar instrument, and the torsion-angle z is observed which is required to set the axis of the magnet perpendicular to the meridian. This operation gives the equation

$$D \sin z = HM.$$

The *ratio* of H to M is found by suspending another magnet of moment M′ in the bifilar, placing the first magnet with its axis in the magnetic meridian through the centre of suspension of the instrument, and determining the torsion-angle z_1, needed to set the suspended magnet perpendicular to the meridian when the north-seeking pole of the first magnet (moment M) is towards magnetic north, and also the corresponding angle z_2, when the north-seeking pole of the first magnet is towards magnetic south. These observations give, subject to the proper corrections, the equations

$$D' \sin z_1 = \left(H + \frac{2M}{r^3}\right) M',$$

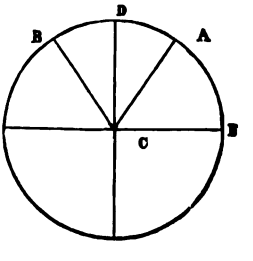
$$D' \sin z_2 = \left(H - \frac{2M}{r^3}\right) M';$$

from which the ratio in question is easily obtained in terms of z_1, z_2, and the distance r between the centres of the magnets. The horizontal intensity is then given by an expression which, when the corrections (for which we must refer to the original paper) are omitted, becomes

$$H^2 = \frac{2D \sin z}{r^3} \cdot \frac{\sin z_1 + \sin z_2}{\sin z_1 - \sin z_2}.$$

V. *On a simple Form of Saccharimeter.* *By* J. H. POYNTING, *Fellow of Trinity College, Cambridge, Professor of Physics in Mason's College, Birmingham.*

THE general principle of the modification of the saccharimeter which I shall describe in this paper is well known, and has already been applied in the construction of several standard instruments, such as Jellett's and Laurent's. This principle consists in altering the pencil of rays proceeding from the polarizer in such a way that, instead of the whole pencil having the same plane of polarization, the planes of the two halves are slightly inclined to each other. The analyzer is therefore not able to darken the whole field of view at once. In one position of the analyzer the one half of the field is quite dark; in another position, slightly different, the other half is dark; while when the analyzer is halfway between these two positions, the two halves of the field are equally illuminated. This will be seen from the accompanying figure.



Let C A be the trace of the plane of polarization of the right half of the pencil, and C B that of the other half. Let C D bisect A C B. Then, if C E represent the plane of polarization of the light which alone the analyzer will allow to pass, when the analyzer is turned so that C E is perpendicular to C A the right-hand side of the field is dark. When C E is perpendicular to C B the right-hand is partially illuminated (as C A has a component along C E), while the left-hand is dark. Halfway between these positions, when C E is perpendicular to C D, both sides appear equally illuminated. The analyzer being turned round till this equality of illumination is obtained, its position is noted on the attached circle. When an active substance is now inserted in the path of the rays, the planes C A, C B are both rotated through the same angle, and the analyzer has to be rotated through this angle to give the equal illumination once more. The circle again being read, the difference of readings gives the rotation due to the interposed substance.

In Jellett's saccharimeter the inclination of the planes of polarization of the two halves of the field is obtained by interposing a prism of Iceland spar. This is formed by cutting a rhomb nearly parallel to its optic axis, reversing one of the pieces, and then cementing the two together again with the plane of separation bisecting the pencil of rays.

In Laurent's instrument, for which homogeneous light is used, half the pencil is passed through a plate of quartz cut with its axis in the surface and parallel to its edge, the thickness being such that the extraordinary is retarded half a wavelength behind the ordinary. On emergence the directions of vibration in the two parts of the pencil, one of which has traversed the quartz, are equally inclined to the edge of the crystal. The inclination of the two to each other can be very easily altered by simply turning the polarizer.

The following arrangement is in place of the Iceland spar in Jellett's instrument, and of the quartz plate in Laurent's. It seems to be somewhat simpler, and gives fairly good results.

A circular plate of quartz cut perpendicular to the axis is divided along a diameter, and one half slightly reduced in thickness. The two halves are then reunited and interposed in the path of the pencil and at right angles to its direction. Since one half of the pencil passes through a slightly greater thickness of quartz, its plane of polarization is slightly more rotated than that of the other half; and the pencil therefore emerges with the planes of polarization of its two halves slightly inclined to each other. It is of course always necessary to use homogeneous light to avoid dispersion.

Mr. Glazebrook has very kindly given me the following numbers, which are taken at random from a large number of sets of readings he has obtained for the electromagnetic rotation of certain solutions of NaCl in water; the difference of thickness of the two plates being ·1 mm., and the inclination of the planes of polarization being therefore about 2° for the sodium-light used. The circle to which the analyzer was attached reads to 3′; but the vernier divisions can easily be further subdivided by eye.

	Circle-readings.
I. Current direct.	23° 45′
	23 46
	23 45
	23 45
Current reversed.	21 36
	21 34
	21 39
II. Current direct.	23 15
	23 16
	23 18
Current reversed.	22 19
	22 19
	22 20
III. Current direct.	23 30
	23 30
	23 28
Current reversed.	21 45
	21 47
	21 48

In order to vary the inclination of the two planes of polarization to each other, one of the halves of the quartz plate might be arranged like a Babinet's compensator, so that the difference of the two might be varied at will. The chief objection to the method seems to be that the quartz plate has to be adjusted very exactly perpendicular to the axis of the pencil.

A still simpler arrangement, which has yet only been tried in a somewhat rough form, consists in a cell containing some active liquid, say sugar solution. This cell is interposed in the path of the pencil; and in it is inserted a piece of plate glass several millims. thick, arranged so that one half the pencil passes through it. This half therefore passes through a less thickness of the active substance than the other half, and is less rotated. The two then emerge as before, having their planes of polarization slightly inclined to each other. This inclination, and consequently the sensitiveness of the instrument can be varied either by varying the strength of the active

solution, or the thickness of the plate of glass inserted in the cell.

This arrangement, as far as it has been tested, gives as good results as the previous one, while it is much more easily constructed and adjusted.

VI. *The Vibrations of a Film in reference to the Phoneidoscope.*

By WALTER BAILY, *M.A.**

[Plate I.]

THE object of this paper is to consider the superposition of several systems of waves in a plane film, when the vibrations are perpendicular to the film, and the wave-lengths of all the systems are the same, with the view of discovering (1) what combinations of systems give simple results in an infinite film, (2) which of these combinations can exist in a finite film, and (3) which of the latter can account for appearances presented in the phoneidoscope.

Let us examine the case of a plane uniform film of infinite extent traversed by three systems of waves with straight fronts, the vibrations being perpendicular to the film, and the wave-length of each system being the same.

Draw (fig. 1) Ac, Bc, Cc meeting in c; and let $\angle BcC = 2\alpha$; $\angle CcA = 2\beta$; $\angle AcB = 2\gamma$. Take $cB = cC = \lambda$. Draw $QcR \perp Ac$; $RBP \perp Bc$; $PCQ \perp Cc$. Join Pc, and draw Qb and Rb, bisecting // PQR and QRP. Draw $ca \parallel Qb$, $cm \perp Rb$, $an \perp Rc$. It may be easily shown that $\angle cab = \alpha$, $\angle abc = \beta$, $\angle bca = \gamma$;

$$cm = \frac{\lambda}{2\sin\gamma}, \quad an = \frac{\lambda\cos\beta}{2\sin\gamma\sin\alpha}, \quad ca = \frac{\lambda}{2\sin\gamma\sin\alpha}.$$

Let λ be the wave-length; Ac, Bc, Cc the directions of the three systems of waves; h, k, l their amplitudes; and d, e, f their phases at some point. The values of $(e-f)$, $(f-d)$, $(d-e)$ are independent of time, and depend only on the position of the point chosen. QR, RP, PQ are wave-fronts; for they are $\perp$ to the directions of the waves.

Consider the line Pc. Every point on this line is equidis-

* Read June 12.

tant from the wave-fronts RP and PQ, so that $(e-f)$ is constant along Pc. Similarly $(d-e)$ is constant along ab, and $(f-d)$ is constant along Rb; and as we may shift the point c, it follows that along any lines $\parallel$ Pb, Qb, and Rb we have $(e-f)$, $(d-e)$, and $(f-d)$ constant respectively. Hence $(f-d)$ is constant along ca.

The value of e at c differs by 2π from its value along PQ, since B$c=\lambda$. Hence the value of $(d-e)$ at c differs by 2π from its value along ab. Similarly the values of $(f-d)$ at b, and of $(e-f)$ at a differ by 2π from the corresponding values along ca and bc.

Now the wave-fronts Rc, cB, BR will reach a simultaneously after crossing distances $= an$. Hence the difference of phase of the whole vibration at c and that at a

$$= \frac{an}{\lambda} 2\pi = \frac{\pi \cos \beta}{\sin \gamma \sin \alpha}.$$

Draw (fig. 2) a series of straight lines $\parallel ab$ at distances $\frac{\lambda}{2 \sin \gamma}$ apart. Along each of these lines $(d-e)$ is constant; and its value changes by 2π in passing from any line to the next. Draw another series $\parallel bc$ at distances $\frac{\lambda}{2 \sin \alpha}$ apart. These lines will have similar properties with respect to $(e-f)$. Straight lines drawn through the intersections of these two series will form a series $\parallel ca$, at distances $\frac{\lambda}{2 \sin \beta}$ apart, and having similar properties with respect to $(f-d)$. At all the intersections $(d-e)$, $(e-f)$, $(f-d)$ have the same values respectively; and therefore at all the intersections the amplitude of the vibration of the film is the same.

We can find a line such that $(d-e)$ is a multiple of 2π, and another line such that $(e-f)$ is a multiple of 2π. At their intersection $(f-d)$ will be also a multiple of 2π. Such a point is a ventral segment. Suppose (fig. 2) the lines to be moved until one of the intersections lies on a ventral segment; then all the intersections are ventral segments.

Now in a Δ with ventral segments at its $/\!/$, let p, q, r be the distances of a point from the sides of the Δ. Let p', q', r' be the differences between the values of $(e-f)$, $(f-d)$, $(d-e)$

at the point and on the respective sides. Then

$$p' : 2\pi = p : \frac{\lambda}{2\sin\alpha};$$

hence

$$p = \frac{p'\lambda}{4\pi\sin\alpha}, \quad q = \frac{q'\lambda}{4\pi\sin\beta}, \quad r = \frac{r'\lambda}{4\pi\sin\gamma}.$$

The displacement of the film at the point at any time may be expressed as

$$h\cos(d+\tau) + k\cos(e+\tau) + l\cos(f+\tau),$$

where τ is proportional to the time after the given moment. The maximum displacement will be

$$\sqrt{\{h^2+k^2+l^2+2kl\cos p' + 2lh\cos q' + 2hk\cos r'\}};$$

that is,

$$\sqrt{\left\{4s^2 - 4kl\sin^2\frac{p'}{2} - 4lh\sin^2\frac{q'}{2} - 4hk\sin^2\frac{r'}{2}\right\}},$$

where

$$2s = h+k+l.$$

This expression vanishes when

$$\sin^2\frac{p'}{2} = \frac{s(s-h)}{kl}, \quad \sin^2\frac{q'}{2} = \frac{s(s-k)}{lh}, \quad \sin^2\frac{r'}{2} = \frac{s(s-l)}{hk}.$$

These values show that there is a node in each triangle the position of which depends on the relative amplitudes of the waves. If one of the amplitudes (say l) is very nearly equal to the sum of the other two, $(s-l)$ is very small, and therefore r' is very small, and consequently r is very small; the result is that the nodes lie in pairs very near together. When one amplitude equals the sum of the other two, the pairs of nodes coalesce; and when one amplitude is greater than the sum of the other two, there can be no node.

In the particular case in which the directions of the waves are inclined at angles of 120° to one another, and the amplitudes are equal, the triangles in fig. 2 become equilateral, with their sides $= \frac{2\lambda}{3}$, and the nodes are equidistant from the ventral segments. Also the difference of phase between successive angles of the triangles is 120°. In fig. 3 let the dots represent the nodes and the numbers the ventral segments.

Then all the *ones* move together, and so do all the *twos*, and also all the *threes*, the difference of phase between the different sets being 120°.

This last case may be investigated algebraically. Let $h =$ the amplitude of each wave, v the wave-velocity, t the time, x, y and r, θ the coordinates of a point in the film, and z the displacement at that point, at the time t. Take a ventral segment as origin, and the direction of one of the waves as axis of x. Then

$$\begin{aligned} h^{-1}z = &\cos\left[2\pi\lambda^{-1}\{vt - r\cos\theta\}\right] \\ &+ \cos\left[2\pi\lambda^{-1}\{vt - r\cos(\theta - 120°)\}\right] \\ &+ \cos\left[2\pi\lambda^{-1}\{vt - r\cos(\theta + 120°)\}\right] \\ = &\cos\{2\pi\lambda^{-1}(vt - x)\} \\ &+ 2\cos\left\{2\pi\lambda^{-1}\left(vt + \frac{x}{2}\right)\right\}\cos(\pi\lambda^{-1}y\sqrt{3}). \end{aligned}$$

When z is a maximum we must have

$$\cos\{2\pi\lambda^{-1}(vt - x)\} = 1;$$

and either

$$\cos\left\{2\pi\lambda^{-1}\left(vt + \frac{x}{2}\right)\right\} = 1, \text{ and } \cos(\pi\lambda^{-1}\sqrt{3}) = 1,$$

or

$$\cos\left\{2\pi\lambda^{-1}\left(vt + \frac{x}{2}\right)\right\} = -1, \text{ and } \cos(\pi\lambda^{-1}\sqrt{3}) = -1.$$

These conditions are satisfied by the sets of values given in the following table; l, m, n being any integers:—

$\lambda^{-1}vt$	$l-\frac{1}{3}$	$l-\frac{1}{3}$	l	l	$l+\frac{1}{3}$	$l+\frac{1}{3}$
$\lambda^{-1}x$	$2m+\frac{2}{3}$	$2m-\frac{1}{3}$	$2m$	$2m+1$	$2m-\frac{2}{3}$	$2m+\frac{1}{3}$
$\lambda^{-1}y\sqrt{3}$	$2n$	$-2n$	$2n$	$-2n$	$2n$	$-2n$

Let Z be the amplitude of the vibration at any point, then Z is the maximum value of z with respect to t. Obtaining this we get

$$h^{-2}Z^2 = \sin^2(\pi\lambda^{-1}3x) + \{\cos(\pi\lambda^{-1}3x) + 2\cos(\pi\lambda^{-1}y\sqrt{3})\}^2.$$

At the nodes $Z = 0$, and therefore

$$\sin(\pi\lambda^{-1}3x) = 0,$$

and

$$\cos(\pi\lambda^{-1}3x) + 2\cos(\pi\lambda^{-1}y\sqrt{3}) = 0.$$

These conditions are satisfied when

$$\lambda^{-1}3x=2m \quad \text{and} \quad \lambda^{-1}y\sqrt{3}=2n\pm\tfrac{1}{3},$$

or

$$\lambda^{-1}3x=2m+1 \text{ and } \lambda^{-1}y\sqrt{3}=2n\pm\tfrac{2}{3}.$$

Putting $y=0$ in the above equations, we get

$$h^{-1}z=\cos\{2\pi\lambda^{-1}(vt-x)\}+2\cos\left\{2\pi\lambda^{-1}\left(vt+\frac{x}{2}\right)\right\},$$
$$h^{-2}Z^2=5+4\cos(\pi\lambda^{-1}3x).$$

The former of these equations gives a section of the film at time t, through a ventral segment in the direction of any one of the waves; and the latter gives a similar section of the surface which encloses the space within which this film vibrates. By putting $x=0$, we get

$$h^{-1}z=\cos(2\pi\lambda^{-1}vt)\{1+2\cos(\pi\lambda^{-1}y\sqrt{3})\},$$
$$h^{-2}Z^2=\{\cos(\pi\lambda^{-1}3x)+2\}^2;$$

and these equations give similar sections to the former ones, but in directions parallel to the fronts of the waves.

The next case we will examine is that of six waves of the same amplitude meeting each other in pairs, the directions of the pairs being inclined to one another at angles of 120°, with the condition that at some one point all the vibrations shall be in the same phase. These may be divided into two sets of three waves each; and the position of the ventral segments of the first set may be represented as in fig. 2. The position of the ventral segments of the second set may be represented by a similar figure, except that we should have to put 2 instead of 3, and 3 instead of 2, in numbering the ventral segments. In superposing the one figure on the other, we must make a ventral segment of the one figure coincide with a ventral segment of the same numeral of the other. Let a *one* of each figure coincide, then all the *ones* will coincide, and will indicate the points of maximum vibration of the film. On the other numerals the film will not have its maximum vibration, as one set of vibrations will partly destroy the other.

We can get a simple algebraic expression for the form of the film.

Divide the waves into two sets as before, and let z_1 be the displacement due to one set, z_2 that due to the other. Then

we have

$$h^{-1}z_1 = \cos\{2\pi\lambda^{-1}(vt-x)\} + 2\cos\left\{2\pi\lambda^{-1}\left(vt+\frac{x}{2}\right)\right\}\cos(\pi\lambda^{-1}y\sqrt{3}).$$

By changing the sign of x and y we turn the whole figure through 180°, and so reverse the motions of the waves; hence we get

$$h^{-1}z_2 = \cos\{2\pi\lambda^{-1}(vt+x)\} + 2\cos\left\{2\pi\lambda^{-1}\left(vt-\frac{x}{2}\right)\right\}\cos(\pi\lambda^{-1}y\sqrt{3});$$

$$\therefore h^{-1}z = h^{-1}z_1 + h^{-1}z_2 = \cos(2\pi\lambda^{-1}vt)\{2\cos(2\pi\lambda^{-1}x) + 4\cos(\pi\lambda^{-1}x)\cos(\pi\lambda^{-1}y\sqrt{3})\},$$

$$h^{-1}Z = 2\cos(2\pi\lambda^{-1}x) + 4\cos(\pi\lambda^{-1}x)\cos(\pi\lambda^{-1}y\sqrt{3}).$$

The results of this equation are represented in fig. 4. The large dots represent the points at which Z is at its maximum, viz. $6h$. They occur when

$$-\cos\pi\lambda^{-1}x = \cos\pi\lambda^{-1}y = \pm 1;$$

that is, when

$$x = 2m\lambda, \qquad y\sqrt{3} = 2n\lambda,$$

and when

$$x = (2m+1)\lambda, \quad y\sqrt{3} = (2n+1)\lambda.$$

The small dots represent points at which $Z = -3h$. Putting this value for Z, the equation becomes

$$0 = \sin^2(\pi\lambda^{-1}y\sqrt{3}) + \{\cos(\pi\lambda^{-1}y\sqrt{3}) + 2\cos(\pi\lambda^{-1}x)\}^2.$$

This is satisfied when

$$2\cos(\pi\lambda^{-1}x) = -\cos(\pi\lambda^{-1}y\sqrt{3}) = \pm 1;$$

that is, when

$$y\sqrt{3} = 2n\lambda, \qquad x = (2m \pm \tfrac{2}{3})\lambda,$$

and when

$$y\sqrt{3} = (2n+1)\lambda, \quad x = (2m \pm \tfrac{1}{3})\lambda.$$

The dotted lines give the locus of points at which $Z = -2h$. Putting this value into the equation, we get

$$0 = \cos(\pi\lambda^{-1}x)\{\cos(\pi\lambda^{-1}x) + \cos(\pi\lambda^{-1}y\sqrt{3})\}.$$

This equation is satisfied when

$$x = (m+\tfrac{1}{2})\lambda,$$

and when

$$x \pm y\sqrt{3} = (2n+1)\lambda;$$

so that the locus consists of three sets of parallel straight lines.

The nodal lines are obtained by putting $Z=0$. The equation to them is

$$0=\cos(2\pi\lambda^{-1}x)+2\cos(\pi\lambda^{-1}x)\cos(\pi\lambda^{-1}y\sqrt{3}).$$

It is obvious from the loci already obtained, that these lines must be closed curves surrounding the points for which $Z=6h$; and that they must approximate to an hexagonal form, the greatest radii being towards the corners, and the least perpendicular to the sides of the hexagons formed by the locus of $Z=-2h$.

Putting $y=0$, we have

$$x=\frac{\lambda}{\pi}.\cos^{-1}.\frac{\sqrt{3}-1}{2}=\cdot381\,.\,\lambda.$$

Putting $x=0$, we have

$$y=\frac{2\lambda}{3\sqrt{3}}\qquad\qquad=\cdot385\,.\,\lambda.$$

These are the values of the greatest and least radii; and therefore the nodal lines are very nearly circles, with radii $=\cdot383\,.\,\lambda$, and centres at the points for which $Z=6h$. The nodal lines are represented by the circles in fig. 4.

We will next consider the case of four waves meeting two and two, the angle between these directions being 2α, the amplitude of all the waves being the same, with the condition that at one point all the waves shall be in the same phase. We have

$$\begin{aligned}h^{-1}z=\;&\cos\left[2\pi\lambda^{-1}\{vt-r\cos(\theta-\alpha)\}\right]\\&+\cos\left[2\pi\lambda^{-1}\{vt+r\cos(\theta-\alpha)\}\right]\\&+\cos\left[2\pi\lambda^{-1}\{vt-r\cos(\theta+\alpha)\}\right]\\&+\cos\left[2\pi\lambda^{-1}\{vt+r\cos(\theta+\alpha)\}\right]\\=\;&4\cos(2\pi\lambda^{-1}vt)\cos(2\pi\lambda^{-1}x\cos\alpha)\cos(2\pi\lambda^{-1}y\sin\alpha).\end{aligned}$$

The ventral segments occur when the quantities have the values given in the following table:—

$\lambda^{-1}vt$	l	l	$l+\frac{1}{2}$	$l+\frac{1}{2}$
$\lambda^{-1}x\cos\alpha$	m	$m+\frac{1}{2}$	$m+\frac{1}{2}$	m
$\lambda^{-1}y\sin\alpha$	n	$n+\frac{1}{2}$	n	$n+\frac{1}{2}$

The ventral segments are divided into two sets: all one set

vibrate together; and all the other set vibrate in the opposite direction.

The nodal lines are two sets of straight lines, whose equations are

$$4x\cos\alpha=(2m+1)\lambda$$

and

$$4y\sin\alpha=(2n+1)\lambda.$$

Hence the nodal lines divide the film into oblongs whose length and breadth are

$$\frac{\lambda}{2\cos\alpha} \text{ and } \frac{\lambda}{2\sin\alpha};$$

and a ventral segment lies in the centre of each oblong. When the directions of the waves are $\perp$ each other, $\alpha=45°$, and the oblongs become squares. This form is shown in fig. 5.

When two waves of equal amplitude meet at an angle $=2\alpha$, the equation is

$$h^{-1}z=\cos\left[2\pi\lambda^{-1}\{vt-r\cos(\theta-\alpha)\}\right]+\cos\left[2\pi\lambda^{-1}\{vt-r\cos(\theta+\alpha)\}\right]$$
$$=2\cos\{2\pi\lambda^{-1}(vt-x\cos\alpha)\}\cdot\cos(2\pi\lambda^{-1}y\sin\alpha).$$

The nodal lines are the straight lines

$$4y\sin\alpha=(2n+1)\lambda.$$

When $\alpha=90°$, we get two waves meeting each other in the same direction. The equation becomes

$$h^{-1}z=2\cos(2\pi\lambda^{-1}vt)\cos(2\pi\lambda^{-1}y).$$

Hitherto we have dealt only with infinite films; we will now consider what forms of vibration can be maintained in films of limited size, the waves undergoing reflection from the boundaries of the film.

When the film is an equilateral triangle, suppose a set of waves to be started having their fronts $\perp$ to one of the sides of the triangle. These waves will be reflected so as to have their fronts $\perp$ to another side, and again reflected so as to have their fronts $\perp$ to the remaining side, and by another reflection they will assume their first direction. If the wave-length is such that the time a wave takes to return to the same position is an integral number of wave-periods, we shall have the case of three sets of equal waves meeting each other at

angles of 120°. Fig. 8 shows the form of vibration when the wave-length is $\frac{3}{10}$ of the side of the triangle (no allowance being made for the change of phase at the reflections). The thin lines show the position of the maximum displacement due to each wave at one of the instants at which these lines all pass through certain points, and the numerals 1, 1 show the ventral segments which are then at their maximum displacement, the ventral segments 2, 2 and 3, 3 come to their maximum at different times, as already explained.

Again, suppose two sets of waves to be started in opposite directions, each set having the front ⊥ to a side of the triangle, and the phases of both sets being the same along a perpendicular from an angle on the opposite side; we shall with a suitable wave-length have six sets of waves meeting each other in pairs, the directions of the pairs making with one another angles of 120°, and all the phases being the same at certain points.

Again, suppose waves to start simultaneously from each of the sides of the equilateral triangle; the waves will be reflected so as to produce other three sets of waves also with their fronts parallel to the sides, by having their direction of motion reversed. Here we again get the six sets of waves above considered, but in a different position. See fig. 6, in which this form of vibration is shown, without allowing for any change of phase at the reflections. The continuous lines show the coincidence of the maximum displacement in one direction due to the waves meeting; and the dotted lines show the same coincidence in the opposite direction. At the black spots we get the coincidence of all the maximum displacements in the same direction; so that these spots show the ventral segments. The wave-length is equal to the distance between the ventral segments $\times \frac{\sqrt{3}}{2}$. With the number of ventral segments shown in the figure the wave-length equals $\frac{1}{3}$ of the height of the triangle when no allowance is made for change of phase at the reflections. The form of vibration of the film is shown in fig. 4, which has been already explained.

We may obtain a similar set of waves in a rhombus having one of its angles $= 60°$, if we suppose sets of waves to start

simultaneously from the four sides, and in each direction from the shorter diagonal.

If in such a rhombus a set of waves starts from the longer diagonal, we get the three sets; and if two sets of waves in opposite directions start from the longer diagonal, we get the six sets.

With a right-angled isosceles triangle we may start a set of waves from the hypotenuse, and so get two opposite sets of waves $\parallel$, and two opposite sets $\perp$ to the hypotenuse; and we may get four similar sets of waves in another position by starting waves simultaneously from the two sides of the triangle.

With a square we can get four sets of waves meeting two and two, the directions being $\perp$ to each other, by starting waves simultaneously from all the sides. In fig. 7 the continuous lines show the coincidence of the maximum displacement in one direction of two waves, and the dotted lines show a similar coincidence in the other direction. The black spots show the ventral segments which move together, and the small circles those which move in the opposite directions. The wave-length = the shortest distance between the ventral segments $\times \sqrt{2}$; and with the number of ventral segments shown in the figure, the wave-length, not allowing for change of phase at the reflections, is $\frac{1}{3}$ of the side of the square.

A similar arrangement of waves in another position may be obtained from a square by starting two sets of waves in opposite directions from one of the diagonals.

To obtain four sets of waves meeting each other two and two, the angles between their directions being 2α, take a rectangle having its diagonals inclined at an angle 2α, and start two sets of waves from one of the diagonals; these will by reflection give two sets of waves with fronts parallel to the other diagonal.

With any rectangle two sets of waves meeting each other can be obtained by starting a set of waves from one side of the rectangle.

The case of two sets of waves meeting each other not in the same direction is impossible in a limited film; and I have not been able to discover any form of film which could maintain three sets of waves not making equal angles with one another,

or six sets meeting in pairs whose directions do not make equal angles with one another.

In the phoneidoscope we have a soap-film thrown into a state of vibration by a musical note. The effect is to send the matter of the film towards the ventral segments, and to make them the thickest part of the film. The consequence is that the colours of thin plates are seen less at the ventral segments than at other parts of the film; and we can recognize the ventral segments in this manner. This effect on the film may be illustrated by M. Decharmé's experiments on Chladni's plates*, in which he shows that if a thin layer of water instead of sand be spread over the plate, the water covers the ventral segments and the nodes are left bare.

The two following experiments may, I think, be explained by what has been said.

(1) A square film, $1\frac{1}{2}$ of an inch in side, was thrown into vibration by a note having 92 vibrations in a second. The position of the ventral segments was that shown in figs. 5 and 7. Hence the vibration of the film was the result of four sets of waves starting simultaneously from the four sides of the film; and the wave-length was approximately $\frac{1}{3}$ of the side; and the wave-velocity was approximately $\frac{1}{3} \times 1\frac{1}{2} \times 92$ inches per second—that is, about 28 inches per second.

(2) An equilateral triangle, one inch in height, was thrown into vibration by a note having 152 vibrations in a second. The position of the ventral segments was that shown in figs. 4 and 6. Hence the vibration of the film may be the result of three sets of waves starting simultaneously from the three sides of the Δ, and giving by reflection three other sets moving in the opposite directions. And the wave-length would then be approximately $\frac{1}{5}$ of the height; and the wave-velocity was approximately $\frac{1}{5} \times 1 \times 152$ inches per second, or about $30\frac{1}{2}$ inches per second. Or the figure may be the result of *one* set of waves starting perpendicular to one of the sides of the triangle (see fig. 8). In this case the wave-length would be $\frac{3}{10}$ of the side of the triangle; and the wave-velocity would be $\frac{3}{10} \times \frac{2}{\sqrt{3}} \times 152$ inches per second, or about $52\frac{1}{2}$ inches per second. As this wave-velocity differs very much from the

* *Ann. de Chim. et de Phys.* sér. 5. vol. xvi. pp. 338–376.

wave-velocity derived from the experiment with the square film, we must reject this latter explanation.

The two experiments may be made to give the same wave-velocity by supposing a change of phase equal to half a period to take place at each reflection. In the first experiment the side of the square has to be taken equal to $\frac{3}{2}$ wave-lengths, and in the second the height of the triangle as equal to $\frac{3}{2}$ wave-lengths. The two expressions for the wave-velocity become $\frac{2}{3} \times 1\frac{1}{2} \times 92$, and $\frac{2}{3} \times 1 \times 152$, both of which expressions are equal to $33\frac{3}{4}$. Hence we are perhaps justified in inferring that the edges are stationary, and that the wave-velocity in the soap-film is nearly 34 inches in a second.

VII. *On a Means to determine the Pressure at the Surface of the Sun and Stars, and some Spectroscopic Remarks.* By EILHARD WIEDEMANN*.

IN a former paper I tried to show that we can calculate, at least approximately, the time elapsing between two encounters of the molecules of a gas by measuring the greatest difference in the length of path at which interference of two rays of light coming from the same source of light is possible. I may be allowed here to quote a passage out of that paper†:—

"Two rays of light can only interfere if they emanate from the same source of light, and if there is no sudden change of phase in the source of light during the time elapsing between the two instants at which the first and second ray leave the source. That difference in phase at which interference is still possible is therefore a measure of the time during which no sudden change in phase has taken place at the source of light. A luminous body sends out light coming from a great number of atoms or molecules. Each molecule will only vibrate regularly as long as it does not come within the sphere of action of another molecule; that is, it will only vibrate regularly in the time elapsing between two encounters. For the different molecules, the time elapsing between two encounters may, according to the molecular theory of gases, be either zero or

* Read June 12th.

† Wied. *Ann.* v. p. 503 (1878); Phil. Mag. [5] vii. pp. 79, 80.

infinitely large. But during a very short fixed time only a small number of molecules will have suffered encounters; only that small number will produce an even illumination of the field of view: the greater number will have vibrated regularly during the whole time; and for all of these interference is possible. The interference-bands in that case are sharp. If, however, the time which we consider to elapse between the emanation of the two interfering rays increases, a greater number of molecules will have suffered encounters, and the bands will therefore be less distinct. It follows that the higher the order of interference-bands, the more diffused and indistinct the bands will be. If the difference of phase corresponds to a difference in time greater than that necessary for the completion of the mean free path, the bands will rapidly disappear, as in that case the greater number of molecules have suffered encounters during the time considered."

Fizeau and Foucault, and, more recently, J. J. Müller and Mascart, have determined the greatest difference of path at which interference is possible. According to the last-mentioned observer, a difference in path of 50,000, and even 100,000 wave-lengths still produces appreciable interference-bands in sodium light. The time corresponding to this difference of phase is about $0{\cdot}5 \times 10^{-10}$ second. Calculating approximately the mean free path (as we only want to compare the orders of magnitude) for hydrogen at 0° and atmospheric pressure, we find for the time necessary to traverse this free path $1{\cdot}14 \times 10^{-10}$ second. The two numbers are sufficiently close to justify the assumption that the sodium atoms may vibrate during 50,000 oscillations without sudden change of phase. We see at the same time that the disappearance of Newton's bands need not be due to the widening of the lines *producing* them.

As the mean time elapsing between two encounters depends chiefly on the pressure, and far less on the temperature, we have a means of determining approximately the pressure of a gas by an examination of the light which it sends out.

The determination of the quantities relating to large difference of paths in the light sent out by the sun, its protuberances, and stars may give us important information on their physical constitution; and I should like to draw the attention of spectroscopists to this point, now that we may soon expect a renewal of the sunspot maximum.

In order to make the measurements, we need only decompose the light we want to examine by means of a spectroscope, separate a ray, which must be as homogeneous as possible, and count the number of Newton's rings visible between two adjustable pieces of glass. We might also determine the thickness of a plate of Iceland spar which still shows interference-bands if it is placed between two Nicol's prisms. The plate must be cut parallel to the axis; and particular attention must be paid to its homogeneousness.

The spectroscopic evidence hitherto has only related to the presence of a substance in the sun; and we only derive from it very general notions as to the physical state. The radiation of heat is, as Janssen has recently again had occasion to observe, a very complicated phenomenon. We must take account of all the different layers on the sun's surface; and the same difficulty besets the interpretation of the Fraunhofer lines. Their thickness and darkness is a function of at least three variables—temperature, pressure, and thickness of absorbing layer; only after having successfully investigated the separate effect of these three variables, will a more perfect interpretation of the phenomena be possible.

If electric phenomena are going on at the solar surface, the difficulty of the ordinary methods of investigation will be still further increased; for, as I have shown,

(1) Very often, if a spark traverses a mixture of gases, one gas only becomes luminous. This result has recently been confirmed by the photographs of H. W. Vogel.

(2) A gas may, by means of an electric discharge, be made luminous below 100° C.

I have concluded from my investigations that the electric discharge increases the oscillatory energy of a gas independently of its translatory motion; and I compared these phenomena to fluorescence.

Hasselberg has confirmed my results, and has drawn some conclusions from them concerning the aurora borealis, comets, &c. I did not in my first communication refer to these matters, as I hoped first to be able to make some experimental investigations in order to fix the relations existing between pressure, luminosity, and quantity of electricity; but I had thought of these evident applications.

The curious forms of prominences which rise and float freely over the solar surface, and which Lohse has tried to refer to chemical processes, may also be explained by electrical causes.

The two results which I have mentioned must render us very cautious before we apply results arrived at by means of the electric arc or vacuum-tubes to solar phenomena. I believe that we cannot at all employ them for the determination of temperature and pressure.

It is by no means necessary that we should have the same relative intensity of the lines in the spectra produced by the two different causes. The effect of the electric discharge is first of all to displace the æther spheres surrounding the molecules; and the vibrations which are caused are in the beginning independent of the translatory motion, which latter chiefly determines the temperature. By means of the encounters of the vibrating molecules the rotatory motion is changed into translatory motion; and then only is the temperature raised so high that the gas may become luminous owing to its heat. This may take place in the narrow parts of a Geissler tube.

If, on the other hand, we produce spectra by means of heating only without calling electricity to help, we first of all increase the translatory motion, which must be increased considerably; for the gas becomes luminous, and then the changes in the forces binding the atoms together to a molecule must affect the spectrum.

At any rate we must carefully investigate the effects of the electric discharge on the nature of spectra before we can draw any conclusions from spectra produced by electricity on questions relating to temperature and pressure. I intend to discuss this point in another paper.

VIII. *On a new Instrument for the Detection and Measurement of Inflammable Gas in Mines.* *By* E. H. Liveing, *Assoc. R.S.M.**

[Plate II.]

The instruments hitherto contrived for the detection of gas

* Read June 26th, 1880.

in mines may be divided under two heads:—1st, those which depend for their action on the *Physical* properties of the gaseous mixture; 2nd, those dependent on its *Chemical* or combustible properties.

Under the former head we have the instruments of Mr. Ansell and Prof. Forbes—the one depending on the diffusion of gases, and the other on the velocity of sound; while under the latter head we have the ordinary flame test, the instrument of M. Coquillion, and, lastly, my own instrument. Strong arguments can be urged to show the superiority of the latter class of tests over those of the former type; for it is the heating-value of the gaseous mixture, or its approach towards the explosive proportion, that we really want to know.

It is quite possible to alter the physical properties of a gaseous mixture to a very large extent while its combustible properties remain scarcely changed. Thus the presence of 6 per cent. of marsh-gas in atmospheric air is sufficient to render it explosive in an upward direction, and there may be present in the mixture amounts of CO_2 from 1 up to 15 per cent. without preventing the mixture being explosive.

Atmospheric air containing 8 per cent. $CH_4 + 8$ per cent. CO_2 is highly explosive; and yet both the instruments above mentioned as dependent on the physical properties would indicate such a mixture as perfectly harmless, indeed would fail to detect the presence of any combustible gas whatever.

There are other drawbacks to these instruments, but I will not occupy your time by detailing them. On turning to the other class we have, first, the flame test. This has, of course, been the practical every-day test employed in collieries for a century or more past, and was applied at a considerable risk before the introduction of the safety lamp, and since that time with comparative security.

The tail or cap observable upon a flame when brought into an atmosphere contaminated with combustible gas is nothing more than a region where the weak mixture of gas and air receives sufficient auxiliary heat to sustain its ignition-temperature, or, in other words, to burn. It is then a direct combustion test, and therefore on the right principle. There are, however, some drawbacks to it: there is a general feeling that it is not sufficiently sensitive; and many hold, further, that

there is a wide difference in the percentage of gas that may be present before the cap makes its appearance. Whether this is correct or not, I am not prepared to give a decided opinion; but, from experiments made, I consider 2 per cent. of marsh-gas about the limit detectable with the ordinary Davy flame. A small and clean flame is an essential requisite in applying this test; any particles of ignited matter on the wick will readily produce a spurious cap when no gas exists.

Of the modes of rendering the cap more visible none is more efficient than turning the flame low, or hiding the luminous portion with some opaque object. Attempts have been made to increase the sensitiveness of this test by viewing the flame through blue glass, with a hope that, the yellow colour of the flame being subdued, the bluish cap would be the more apparent; but this has failed practically to increase the sensitiveness of the test, and, I believe, for this reason—that as the percentage of gas is diminished the cap decreases more in size than in intensity; for it is only those molecules that come into very close proximity to the flame that obtain sufficient auxiliary heat to enable them to reach the ignition-temperature.

Of the instrument of M. Coquillion I have nothing to say; for though it may be a very convenient and neat apparatus for gas-analysis, the fact that it cannot be employed in the pit, and that samples of air have to be brought to it puts it entirely out of the present question.

I now come to my own instrument. The principle on which it is based is as follows:—A mixture of marsh-gas and air in which the marsh-gas forms less than 5 per cent. of the mixture is not explosive or capable of continuing its own combustion (at ordinary temperatures and pressures), simply because the heating-value of the CH_4 is insufficient to raise that large excess of atmospheric air to the necessary ignition-temperature. If, however, such a mixture is exposed to some sufficiently heated object, especially if that object is platinum, it will burn in its immediate contact and neighbourhood, and in so doing add materially to the temperature of the object, and the more so the larger the percentage of gas present. To apply this principle to

the detection and measurement of gas in the air of mines, I have contrived the following arrangement (shown in Plate II.) :— A and B are two spirals of very fine platinum wire, through which a current from a small magneto-electrical machine is made to circulate. Both wires being in the same circuit, and offering equal resistances and cooling-surfaces, become equally heated on turning the machine; one of these spirals is enclosed in a small tube having a glass end and containing pure air ; the other is exposed within a small cylinder of wire gauze (also with a glass end) to whatever gaseous mixture is drawn within the instrument for examination.

So long as the air examined is free from combustible gas or matter, the two spirals glow with an equal brilliancy; but if the air contain any amount above $\frac{1}{100}$ of its volume of CH_4 the exposed spiral increases in brilliancy, and the more so the nearer the percentage approaches the explosive proportion; and this difference of brilliancy becomes a means of determining the percentage of gas present.

To measure the difference of brilliancy there is a simple form of photometer, consisting of a small wedge-shaped screen C, the two surfaces of which are covered with paper and illuminated, the one by the covered spiral, the other by the exposed one. These two surfaces are viewed through the small side tube G, which, together with the screen and outer tube K, can be moved towards the covered spiral until equal illumination of the two surfaces of the screen is attained in the particular gaseous mixture under examination. An empirical scale is then read off, which gives at once the percentage of gas present.

The following table shows the difference of brilliancy due to stated percentages of CH_4; but the amount much depends on the size of the wires, proportion of the spiral, and other conditions, and can only be determined by actual trial in known mixtures. It is a point worthy of note that the rate at which the machine is turned does not seem to have any sensible effect on the ratio of brilliancy of the spirals so long as the exposed one is heated to the igniting-point of CH_4.

Table of observed Illuminating-power of the Spirals in different percentages of gas.

Per cent. CH_4.	Relative illuminating-power of spirals.	
	Covered spiral.	Exposed spiral.
Pure air.	1	1
½ per cent. CH_4.	1	1·24
¾ " "	1	1·65
1 " "	1	2·78
2 " "	1	5·1
3 " "	1	22
4 " "	1	64

When moderately large quantities of gas are present, such as two or three per cent., the difference in colour of the light emitted by the two wires becomes so striking as to cause some difficulty in judging of the exact position of equal illumination of the screen, a difficulty of course felt more or less with all photometers when examining lights of different tint. This difficulty is avoided (so far as the object of this instrument is concerned) by covering one half (Y, fig. 2) of that side of the screen that is illuminated by the exposed spiral with yellowish red paper, the other half, X, remaining white; and for quantities below 2 per cent. the white surface X is compared with the white surface Z; but above that amount the yellow surface Y is employed, its tint neutralizing the very white light of the exposed wire and rendering the comparison easy.

I must now say a few words relative to the practical use of the instrument.

In the modern systems of colliery-ventilation the main current of air that descends the downcast shaft is soon subdivided into several separate currents (or "splits," as they are called). These, passing along the principal travelling-ways, are conveyed to the different districts where the men are working, and, after ventilating a certain number of working-places and becoming more or less contaminated with the combustible gas that is there evolved from the freshly exposed surface of the coal, are carried by air-ways known as "returns" to the upcast shaft, often skirting in this part of their course large areas of broken ground (or goaf) where the coal has been entirely removed.

Now it is for the examination of the air passing in these different returns that I consider this instrument specially adapted, as it at once enables the manager of a colliery to determine the quantity of gas evolved in the different working-districts, and thus regulate the proportion of his various currents of air so as to make the best use of the given ventilating-power that he has at his disposal, and not have some of his air-ways considerably contaminated with gas whilst others are practically free (a condition I have frequently found to be present). Again, if a regular account of the observed percentages of gas be kept, the quantity of air passing and the barometric pressure being also noted, it will soon become evident within what limits it usually varies; and should at any time an abnormal increase be observable, it will be desirable to follow up the return until the source is ascertained and precautions, if necessary, taken.

The instrument thus employed, and the results carefully considered, cannot fail to be of assistance in laying out and regulating the ventilation of extensive collieries. There is, however, another and perhaps more urgent requirement which I hope a slight modification of this instrument may also be able to meet.

There exist many gassy collieries where safety lamps are alone employed, and yet where the hardness of the coal necessitates the use of powder in order that it may be worked at a profit. Now in such workings, before each shot is fired, it is necessary for the sake of safety (and enforced by the Coal-Mines Regulation Act) that the working-place and its neighbourhood should be carefully tested for gas. This is of course done at present by aid of the lamp, and, it is to be feared, too often without that degree of care and deliberation by which alone the test can be considered efficacious. Be this as it may, all are agreed that some more striking and definite test would be of great value for this purpose, if it could be practically introduced.

For this object I propose a slight modification of the instrument described, in which the screen is fixed at some definite percentage, such as 2 per cent., the one side being marked G, the other A; the directions for use being that so long as the

side A of the screen is the brightest the shot may be fired, but if G become equal to or brighter than A the shot should not be fired.

For this purpose the instrument and machine would be best made in one piece, and would have to be constructed as *strongly*, *simply*, and *cheaply* as possible, with an easy means of replacing the platinum spirals, should they be melted through carelessness.

I may add that the chief difficulty about the introduction of the instrument is to find a sufficiently compact and portable source of the necessary electrical current that can be made at a moderate price.

There is yet one other possible application of the instrument —namely, for the examination of the heating-value of the waste gases from blast-furnaces, where it is of importance to regulate the conditions of burning so as to reduce the carbonic oxide in the waste gases to a minimum. Of course the sample of waste gas would have to be mixed with some definite quantity of air, to supply oxygen, before examination.

EXPLANATION OF PLATE II.

R and S are two strong brass plates that form the terminals of the electrical machine and at the same time act as supports for the instrument.

D and E are wooden plugs with copper wires carrying the platinum spirals A and B; these are arranged so as to be easily replaced in case of accidental melting or damage. For this purpose the thumb-screws L and M are removed, and the whole instrument turned half round upon the screws O and P; the plugs being in this position released, can be replaced by fresh ones, two small springs making the requisite contacts without trouble. The path of the current is shown by arrows.

There are two small entrance-tubes, through which a breath is taken to fill the instrument with the air to be examined. These are not shown in the figure, not being in the plane of section.

Q is the magneto-electrical machine, the dimensions of which are $8 \times 5 \times 1\frac{3}{4}$ inches.

IX. *On the Behaviour of Liquids and Gases near their Critical Temperatures.* *By* J. W. Clark.

[Plate III.]

In 1822 Baron Caignard de la Tour * showed that the effects of heat on a liquid enclosed in a vessel adapted to the purpose, was to convert it into vapour at a volume a little more than twice that which it originally possessed. Within a certain limit he found the temperature at which this change occurred was independent of the ratio existing between the volume of the liquid and that of the tube, but above that limit the conversion was first observed at a higher temperature. Brünner †, after an extensive discussion of previous memoirs, states the results of his observations upon the decrease which heat produced in the height to which water, ether, and olive oil rose in capillary tubes. He experimented at temperatures below 100° C. In 1857, from Brünner's expression for this decrease in the case of ether, Wolf ‡ calculated the temperature at which the level of the liquid in the capillary tube should coincide with that outside it; and in the attempt to test his conclusion experimentally he found that it sank below the liquid in the external tube. He stated that the surfaces became convex, and that the depression was the result of true capillary action, as in the case of mercury. Drion § then took up the subject, and ultimately came to the conclusion that the depression of the liquid in the capillary tube just before its vaporization was the result of a less rapid expansion produced by a difference of temperature too small to detect with a thermometer. He described the surface of the liquid at the moment of disappearance as perfectly plane, and the apparent convexity as the result of refraction.

Mendelejeff ‖ appears to have misunderstood Wolf; for in 1870 he writes :—"Wolf hat im Jahr 1858 (*Ann. de Chim. et de*

* *Ann. de Chim. et de Phys.* t. xxi. p. 127 and p. 178; *ibid.* t. xxii. p. 411.

† Pogg. *Ann. der Phys. u. der Chemie*, Bd. lxx. S. 481.

‡ *Ann. de Chem. et de Phys.* t. xlix. p. 272.

§ *Ann. de Chim. et de Phys.* 1859, p. 221; and *Comptes Rendus*, t. xlviii 1859.

‖ Pogg. *Ann.* 1870, Bd. 141, S. 621.

Phys., t. 49, p. 259) gezeigt dass bei der Temperatur bei welcher Aether in zugeschmolzenen Röhren ganz in Dampf verwandelt wird der Meniscus verschwindet und dass Niveau des Aethers in der Capillarröhre und in der weiten Röhre gleich ist. Die Beobachtung wurde von Drion (*ibid.* 1859, t. 56, p. 221) bestätigt und erweitert." The researches of Dr. Andrews * are too well known to need special reference here; and the discussion of a paper by Dr. Ramsay†, on the "Critical State of Gases," will be best left until the completion of the work in part described in this paper. Messrs. Hannay and Hogarth ‡ have recently shown that under certain conditions solids may be dissolved in gases. Unfortunately, Mr. Hannay's paper, "On the Cohesion Limit," recently communicated to the Royal Society, is not yet printed; so that reference to it must be left until a future occasion.

In December 1878 I read a short preliminary note before the Society, "On the Surface Tension of Liquified Gases," in which the results of some measurements on sulphurous anhydride at low temperatures were given §. Last year, at the Society's meeting at the Royal Indian Engineering College in June, a curve showing the height at which sulphurous anhydride stands in a tube at temperatures between −17° C. and the critical temperature was shown, and the depression of the liquid in a capillary tube, with some unsuccessful attempts to determine the cause of it, were described. As this is the last meeting of the session, I beg leave to lay the result of the inquiry before the Society.

Two methods of heating will be noticed in this paper. The first consists merely in heating a large test-tube of oil over a rose gas-burner, the experimental tube being suspended vertically in its axis a little above the bottom by a fine platinum wire. Numerous experiments have been tried with U-tubes of which the branches were of *equal diameter and glass-thickness*;

* Phil. Trans. 1869, p. 575; *ibid.* 1876, p. 421.

† Proc. Roy. Soc. vol. xxx. p. 323.

‡ *Ibid.* xxix. p. 324; *ibid.* xxx. pp. 178 and 188.

§ I have since found that the value then given is considerably too low, no correction for the diameter of the external tube having been made. To Professor Quincke I am greatly indebted for having directed my attention to the previously reasoned observations of Wolf and Drion here quoted, and for having kindly supplied me with most of the above references.

and the results show that the heating, although rapid, is nearly, if not quite, uniform. It is worth notice, however, that at temperatures very near the critical, the density of liquid and vapour are so nearly equal that when the heating is made unequal, the entire disappearance of the liquid from one branch of the tube does not affect its level in the other. The second method of heating is more complex, but has answered the purpose sufficiently well to deserve brief description. In the middle of a four-litre beaker of oil* is fixed a round-bottomed thin flask of 1·5 litre capacity. The neck, which is about 3 centims. in diameter, is thickly wrapped round with cotton wool and calico, and is long enough to rise 7 centims. above the perforated cover which closes the beaker. The beaker rests on wire gauze carried by a large iron ring, and is surrounded by a tin cylinder 8 centims. wider than the beaker, furnished with two small glass windows on opposite sides. The neck of the flask passes through the cover of this outer case, and is closed air-tight by an indiarubber cork, through which the bulb of a long-stemmed thermometer is inserted. Just below the cork is fused into the neck a narrow glass tube connected with a slightly modified Bunsen regulator (fig. 1, Plate III.) by a short piece of composition pipe (*a*) 2 millims. in diameter†. The other end communicates through a short glass tube (*b*) with the air-mercury bulb of the usual regulator. A small glass stop-cock (*c*) serves to place the flask and regulator-bulb in communication with the air. A large rose burner protected from air-currents heats the beaker of oil.

When the apparatus is in use the experimental tube is suspended in the middle of the flask by a thin wire, the glass stop-cock (*c*) of the regulator opened, and a small gas-flame lit beneath the beaker. When ether is used in the experiment, in from eight to ten hours the temperature rises to within

* The best salad oil heated out of contact with such metals as copper and iron will bear repeated heating to 200° C. It ultimately becomes thicker and denser, and exhibits a green fluorescence. By long exposure to the action of air and light, particularly in thin sheets, it regains its transparency and again becomes fit for use. It should be noticed that some sorts of glass are violently attacked by hot oil.

† These regulators may be obtained from Mr. Bel, 34 Maiden Lane, Strand.

three or four degrees of the critical; the glass stop-cock (*c*) is then closed, and the pressure of the expanding air in the flask begins to raise the mercury until it meets the platinum tube (*e*) of the regulator, which is previously screwed down till within about 3 millims. of the surface of the mercury. Some two or three hours later the critical temperature is reached. The light from a paraffin lamp passes through a cylindrical lens, and enters through one of the glass windows in the case enclosing the apparatus, thus rendering the experimental tube visible through the other window. The observations are made with a cathetometer-telescope.

Early in this inquiry it was found that so many circumstances influenced the depth to which the liquid was depressed in the capillary tube, that two different tubes could be satisfactorily compared only when enclosed in the same external tube; and if the effects of slow and rapid heating are to be compared, the tubes should be of the same thickness of glass. Small springs of thin platinum (S, fig. 2) fix the capillary tubes vertically in the axis of the external tubes, which latter have been employed of various diameters between 2 and 20 millims. When the slow heating-apparatus is used, the experimental tube (enclosing the capillary tube) is fixed in the axis of a tube of considerably greater diameter, which is then exhausted of air and hermetically sealed (see fig. 3). Ether distilled from calcic chloride has been the liquid most frequently employed; but, so far as I am aware, all the results about to be described are also obtained with alcohol, sulphurous anhydride, and carbonic disulphide. Water attacks glass so rapidly that it is difficult to ascertain what is taking place in the tube; but it probably forms no exception to the liquids mentioned.

After the introduction of the capillary, the external tube is filled with liquid, and the air removed as completely as possible by repeated boiling, and the volume of the liquid is reduced to a convenient extent. When such a tube contains ether and is heated, the liquid sinks in the capillary tube and rises in the outer, the expansion becoming more and more rapid as the critical temperature is approached. About 2° C. below this temperature the meniscus in the capillary tube stands at the same level with that in the external tube. Both surfaces are then distinctly concave. In the case of alcohol

the temperature at which this is observed is *probably* a little more, and for sulphurous anhydride a little less, than 2° C. below the critical temperature. The exact temperature is affected by a number of circumstances: thus it is lower with a wide capillary tube than a narrow one, and for the same capillary tube it is also lower when this tube is deeply immersed in the liquid. Continuing the heating, the meniscus (*c*) in the capillary is seen below that (C) in the external tube (fig. 4). It then gradually loses its concavity, becomes successively plane and less defined, and frequently presents a more or less convex appearance before finally vanishing. Meanwhile the liquid in the external tube expands and undergoes the same changes, the defined surface appearing more or less convex, and then becoming black and ill-defined. It first ceases to be visible in the capillary tube. The curve fig. 5, Plate III., shows the changes in the height of liquid sulphurous anhydride in a capillary tube of 0·4358 millim. diameter in an external tube 3·2 millims. wide. The abscissæ are in degrees centigrade, the ordinates in millimetres. The measurements near the critical temperature could only be made with difficulty, and are consequently less reliable than those made at a lower temperature. Measurements of the *depression* of the liquid, or even of the diameter of the capillary tube in which the depression is observed, possess but little value, other conditions (*e. g.* rate of heating, &c.), incapable of exact expression, exercising too great an influence upon it. When the tube is rapidly cooled a local cloud of very fine particles suddenly makes its appearance, in the middle of which the liquid first appears as a fine horizontal line (fig. 4). In the capillary tube this cloud extends to a considerably greater distance, both upwards and downwards, than in the external tube. Probably this is connected with a surface-action, to be described subsequently. The mean position of the cloud is nearly that at which the tube-contents disappeared on heating. The formation of this cloud reminds one forcibly of the sudden crystallization of a supersaturated solution. The volume which the liquid then first occcupies is less than that which is possessed before its disappearance, and is considerably less if the black ill-defined surface visible on heating be taken into consideration. A persistent tendency on the part of the ether and sulphurous

anhydride gases to condense at a lower temperature (particularly when somewhat rapidly cooled) than that at which they were formed is very noticeable *. Rapidly cooled (especially in narrow external tubes) the liquid, when it first becomes visible on condensation, is either level in the capillary and external tubes, or higher in those tubes in which the depression on rapid heating has been the greatest. When slowly cooled, or even when somewhat rapidly cooled in an external tube of large diameter, the liquid condenses in greater quantity in the external tube than in the capillary tube, and hence the liquid has to rise in the capillary tube before it reaches the level of the liquid outside. This is easily seen to be the case from the shape of the condensing cloud in an external tube 20 millims. in diameter. It will be subsequently seen that the resistance which the narrow tube offers to the flow of the liquid through it, is at least very closely connected with the cause of the depression †.

When the tubes are very slowly heated in the apparatus already described, the above phenomena are considerably modified. The volume occupied by the same liquid before its vaporization is then seen to be far greater than that occupied by it when rapidly heated. To illustrate this the volume of ether in a certain tube at the ordinary temperature was roughly 25. Rapidly heated, the volume at which the *liquid* disappeared was between 35 and 40; and at a volume of about 45 the last traces of black cloud had gone and the contents of the tube appeared perfectly homogeneous. Slowly heated when the liquid had expanded to a volume of 52, the meniscus was slightly, but perceptibly, concave, and disturbed by a rising bubble of gas. The enclosed capillary tube was not long; and the liquid expanded until it reached the top, and then poured into the tube and filled up the existing depression. Indications that a higher temperature is required for this in-

* Although it is premature to draw any definite conclusion from this, it may be of interest to recall the researches of Magnus (Pogg. *Ann.* xxxviii. 592), and Regnault (*Mémoires de l'Académie* 1862, xxvi. 715–749, 335–664) on the vapour-pressures of liquid mixtures, which seem to bear a possible relation to it. In this connexion see also Cailletet's paper (Phil. Mag. March 1880, p. 235).

† For this idea I am indebted to a suggestion made to me by my friend Mr. Eagles.

creased expansion of the liquid have been observed; but whether the temperature at which the liquid disappears is the same for rapid and slow heating has not yet been satisfactorily determined. Continuing to heat, the liquid expands, and the surface is reduced to a thin and often waving line, obliterated by further expansion, or lost amongst the frequent striæ. Under these circumstances the volumes of disappearance and reappearance are nearly equal, and the corresponding temperatures sometimes differ by less than 0°·1 C. A very slight sudden rise of temperature, when the liquid has expanded beyond the volume at which it disappears under rapid heating, suffices to replace the defined surface by the black ill-defined one before described; but, apparently, when this expansion has proceeded too far, the surface then becomes broad and ill-defined, but not black. It then passes from the liquid through this ill-defined state without expansion; and the liquid in a rather wide capillary tube is then seen to be level with that outside it. Slowly cooled, the tube frequently becomes uniformly filled with striæ, and the light transmitted through the experimental tube by the paraffin lamp before described is observed to become gradually redder and redder. This is succeeded by the formation of a whitish incipient cloud, which finally precipitates in visible particles, often throughout the whole tube. The liquid contracts from the first moment of its condensation until it regains its original volume. Slow and regular cooling seems more difficult to attain than the corresponding conditions on heating.

When the external tube contains rather less ether than the above—that is, when about one third filled, and rapidly heated, the liquid expands and passes into gas in the usual way. Very slowly heated the liquid also expands; but after reaching a certain maximum volume, it very gradually diminishes and evaporates away. If the volume of liquid at its point of maximum expansion happens to be such that the liquid in the external and capillary tubes are almost level, the meniscus in the capillary tube shows a slight tendency to increase its height above the surface when the contraction commences. A slight sudden rise of temperature produces a result similar to that described in the last case. On cooling, the liquid in such a tube undergoes a momentary and almost inappreciable increase of volume just after condensation, and

then contracts to its initial volume as in the previously described tubes. If a tube contains still less ether than the last mentioned, the liquid undergoes a more marked increase of volume when it first condenses; and this continues longer before the normal contraction sets in.

Very near the critical temperature the density of liquid and gas are almost equal; and hence it is that the meniscus in the capillary tube may remain depressed for as much as an hour and a half, although very slowly following the upward motion of that in the external tube. The meniscus in the capillary tube usually fades away a little before the surface ceases to be visible in the external tube. This may be due to its being under a slightly lower pressure.

The meniscus in a wide capillary tube is observed below the surface of the liquid in the external tube before that in a capillary of small diameter; and rapidly heated, the depression usually remains greater in the wide tube until the surface ceases to be visible. This disappearance frequently takes place first in the small, then in the larger capillary, and lastly in the external tube; when the heating is sufficiently slow, the depression becomes greatest in the tube of small diameter. Slow or rapid heating and slow cooling alike show the depression is greater in a tube roughened by hydrofluoric acid than it is in a smooth one of the same size. When the heating is rapid, the depression in a capillary tube the immersed half of which has been previously heated and drawn out until the diameter is very small is less than it is in the corresponding tube of uniform diameter throughout. Slow heating reverses this result, as shown in fig. 3. By the mere contraction of the extreme end of the immersed part of a capillary tube the depression is almost uninfluenced. The results above described are not invariable (and some points connected with them are still the subject of inquiry); but under conditions which are apparently the most free from error they become sufficiently so to justify their being regarded as normal.

It seems probable that the effects of unequal and irregular heating are completely removed from the above experiments; for the liquid is equally depressed in two capillary tubes of equal diameter, one made of very thick, and the other of very

thin glass. Rapidly heated, the depression reaches a maximum in the thick glass tube. Of two similar capillary tubes the most deeply immersed always shows the deepest depression; but the length of the tube above the liquid is apparently without influence. This led to the result described to the Society in June 1879, viz. that when the capillary tube does not dip more than a millimetre or two below the surface the liquid disappears at the same level in the capillary and external tubes.

It has been previously stated that the liquid sometimes appears convex near the critical temperature. With ether in a tube 20 millims. in diameter, this apparent convexity is so well marked that I had at first much difficulty in satisfying myself that such was not the case. By means of a lamp, cylindrical lens, and slit, a bright line of light is easily thrown into the liquid in such a tube heated in a large beaker of oil. The changes in the form of the reflected image were then observed; and from this it was inferred that when the liquid surface appears convex and well-defined, as seen through the horizontal telescope, it is slightly but unmistakably concave, and remains so until it loses the power of reflecting when it is plane. This apparent convexity is caused by the raising of the far edge of the liquid by refraction; or perhaps it may resemble mirage, as I have distinctly seen the *surface* of the liquid in the horizontal telescope. The surface subsequently becomes black and ill-defined, and, as Professor McLeod has pointed out to me, closely resembles the surface of alcohol and water in a test-tube into which they have been carefully poured so as not to mix. The band of light which leaves the cylindrical lens, and passes through the vertical tube of ether, gives rise to some remarkable refraction figures at the surface of the liquid. By substituting the test-tube of alcohol and water for the tube of ether, corresponding figures are obtained—heat in one case, and diffusion in the other, causing these figures to pass through the same changes. It appears possible that the black surface may be due to the mixing of the liquid ether with its vapour when they are of nearly equal density. This view receives some support from the fact that, just before the defined surface of the liquid is lost, the convection-

currents become so rapid and violent as to disturb and apparently almost break through it into the vapour above.

The above conclusion as to the form of the surface receives confirmation from some experiments with an external tube enclosing two glass plates 0·15 millim. thick, and 11 millims. wide, and separated from each other by a short distance. Not the least rounding of the surface of the liquid could be detected either between or around the plates. That no depression of the liquid was observed between the plates, corresponding to that in the capillary tubes, may be explained by the very small expansion of the liquid in this tube at that point at which the depression usually takes place. Under the same conditions the depression is absent also from a capillary tube. The expansion, as already stated, is dependent upon the amount of liquid in the tube and upon the rate at which it is heated. On cooling, just as the cloud appeared, and before the liquid line had made its appearance in it, an interesting action was observed taking place on the surfaces of these glass plates; for, extending downwards into the cloud and considerably aoove its upper limit, a liquid film could be seen running over their surfaces. This probably affords evidence of a surface-action preceptibly influencing the position at which the condensation of the liquid takes place.

It remains only to briefly notice a class of facts to which reference has not yet been made, but which includes certain conditions capable of modifying some of the results described in a part of this paper. It has been very frequently observed that when a tube is heated for the first time, the depression is smaller than it is when the tube is again heated within a short time of the first experimnnt. In a few capillary tubes the liquid is seen to disappear at the same level as the liquid outside them; but reheating shortly after the liquid has condensed, the usual depression is observed. When such a tube has been left a sufficient length of time in contact with the liquid on heating, the same result is obtained as at first; this may be repeated indefinitely. For two tubes this time has been determined, and in both cases found to be about 20 hours; a shorter period merely sufficed to *diminish* the depression. Probably closely connected with this action is the gradual

decrease Quincke * has observed that time produces in the form of a bubble of gas in a liquid, and of a drop of mercury. To this class of facts are also nearly related the decrease in the intensity of Quincke's † electrical diaphragm-currents, and that which ‡ I have shown to take place in the electromotive force produced when water is forced through capillary tubes. Elster § has recently extended the observation to a similar variation in the electromotive force set up by liquids flowing over the surfaces of solids. Dorn‖ has investigated at some length the cause of this action in the case of tubes, and has shown that it is capable of modification in various ways, some of which appear capable of exercising a corresponding control over the above-described depression of a liquid in a capillary tube at a temperature near the critical.

It is proposed to continue the still incomplete portions of this inquiry in a paper to the Society next session.

In conclusion I beg leave to express my thanks to Professor McLeod, not only for having advised me to extend my observations to higher temperatures than those at first employed, but also for the willingness he has always shown to aid me with valuable suggestions.

Summary of Contents.

1. When a tube enclosing a capillary tube dipping into alcohol, ether, or sulphurous anhydride is heated, the liquid sinks in the capillary, and rises by expansion in the outer tube. Between 2° and 3° C. below the critical temperatures of these liquids both surfaces become level; and on continuing to heat, the concave meniscus in the capillary tube is seen below that in the external tube. The extent of this depression depends on the diameter &c. of the capillary tube, and on the nature of its internal surface. When the end of a capillary tube dips very slightly below the surface of the liquid, it is level in the capillary and external tubes at the disappearance of the liquid.

* Pogg. *Ann.* Bd. clx. S. 576. † *Ibid.* Bd. cx. S. 56.

‡ *Ibid.* 1877, S. 345.

§ *Inaugural-Dissertation über die in freien Wasserstrahlen auftretenden elektromotorischen Kräfte.* Leipzig, 1879.

‖ Wiedemann's *Ann.* Bd. ix. 1880, S. 523. Compare also Helmholtz, Wied. *Ann.* vii. p. 337 (1879).

2. In some capillary tubes the liquid is not depressed, but disappears at the level of the liquid in which they are immersed on first heating. Once heated, long contact between liquid and tube is necessary to prevent the formation of the depression on again heating. For two tubes which were examined, this time was in each case about 20 hours; a shorter period merely sufficed to *diminish* the depresion. The depression is the result of an action between the liquid and the inner glass surface of the capillary tube.

3. Indications that surfaces exercise a slight action in determining the position at which the liquid condenses in the external tube have been observed.

4. By reflecting a bright line of light from the apparently convex and well-defined surface of ether in a tube of 20 millims. diameter at a temperature near the critical, it may be inferred to remain concave until it loses the power of reflecting when it is plane. The apparent convexity is the result of refraction, or, perhaps, of an action resembling mirage.

5. The black ill-defined band which immediately succeeds the disappearance of the liquid surface is the result of too rapid heating, and possibly due to the mixing of liquid and vapour when they are of nearly equal density. When very slowly heated, as described, the defined concave surface is gradually obliterated, and is last seen as a fine and often waving line. Under this condition also the volume of the liquid at its disappearance is greater than when it is rapidly heated. When the liquid is vaporized by rapid heating, it has a higher temperature and larger volume at the time of disappearance than it has when first condensed by cooling; slowly heated and cooled, these volumes and temperatures are more nearly the same.

Royal Indian Engineering College,
June 1880.

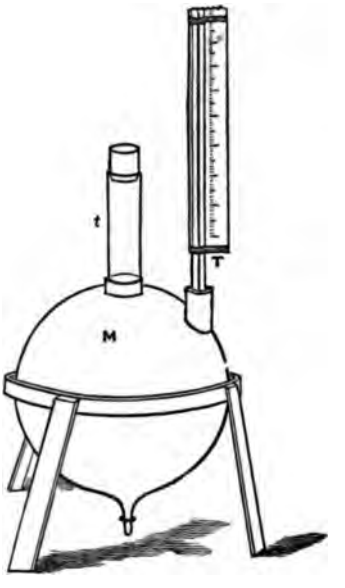
X. *Note on a Modification of* Bunsen's *Calorimeter.*

By W. W. Gee *and* W. Stroud*.

Professor Stewart described to the Manchester Literary

* Read June 26.

and Philosophical Society, on March 4, 1879, a calorimeter devised with the purpose of obtaining the specific heat of a substance of small quantity with much readiness. It consists of a combination of part of Bunsen's arrangement with that of Favre and Silbermann. In it advantage is taken of the method employed by Bunsen—namely, that of dropping a small body, whose temperature does not differ much from that of the atmosphere, into ice-cold water contained in a small tube. In Bunsen's instrument the heat so given up by the body experimented with is measured by the change of volume produced by the melting of ice surrounding the tube. There being certain practical difficulties in the use of this method, it was thought that if the tube were surrounded by a large mass of mercury, forming the bulb of a delicate thermometer, after the manner of Favre and Silbermann, then the direct expansion of the mercury would indicate the amount of heat brought into the tube by the body, this mercury being in its turn surrounded by melting ice not in contact with it. The instrument figured was made by Casella. T is the graduated tube of a glass thermometer whose large bulb is encased in the copper chamber M, there being only a small air space between the two. In the centre of this large bulb a test-tube *t*, provided with a cork, is tightly inserted, so that its lower portion is completely surrounded by the mercury in the bulb.



Prof. Stewart intrusted the calorimeter to us, in order that we might determine its working conditions and ascertain how far it was reliable.

The following was the way in which the apparatus was tested. The test-tube was first filled with water to the level of the mercury inside the

bulb. The instrument being placed in its wooden case, the latter was then filled with pounded ice and then allowed to cool down until the column of mercury in the stem of the thermometer T was apparently stationary between two observations taken at an interval of about fifteen minutes.

After preliminary trials with various quantities of mercury dropped into the test-tube, it was found absolutely necessary to make some allowance for the loss of heat from the surface of the mercurial thermometer by radiation and convection; for although the rise produced by dropping in was almost immediate, yet during a comparatively long period of apparent maximum that followed, the heat received must have been equivalent to the heat lost by radiation and convection. (This prolonged stationary period, it was always observed, was followed by a comparatively rapid fall.) A curve of cooling, extending from 0°·3 to 0°·0 C., was accordingly obtained, with times as abscissæ and temperatures as ordinates. By aid of this curve the loss of heat was allowed for by a simple method of compensation.

Brass and mercury were selected for comparison. The results, after applying the correction above indicated, for 2 and 6 grams of mercury and 2 grams of brass are given below:—

2 grams	mercury	at 15°·8 C.	Corrected rise		15·6
2 „	brass	at 15°·9 C.	„	„	46·0
6 „	mercury	at 15°·25 C.	„	„	48·5

An inspection of these results, knowing that the specific heat of brass is about three times that of mercury, will show that the principle of the instrument is experimentally verified. The bore of the thermometer-tube being, unfortunately, large, necessitated a small rise; greater accuracy hence could not be expected. It is hoped shortly, however, to make further experiments with a new instrument having a much smaller bore, and with other needed improvements that could not in a first instrument be foreseen as wanting.

XI. *On Magneto-Electric Induction.*—Part II. *Conductivity of Liquids.* *By* FREDERICK GUTHRIE *and* C. V. BOYS, *Assoc. R. Sch. Mines**.

[Plate IV.]

IN a previous communication † we showed experimentally that, other things being equal, a conductor in a moving magnetic field is urged to move by a force which varies as the product of the conductivity into the relative speed; so that by observing the torsion of a wire supporting successively a variety of conductors of the same form and size in a revolving magnetic field, a measure of their relative conductivity may be obtained. In the case of most metals, this method of determining conductivity cannot be compared, at least for convenience, with the usual one with the bridge, galvanometer, &c.; but with less-perfect conductors, with such as cannot be drawn into wire, and especially with electrolytes, our method seemed very promising; for, whatever be the actual course of the electrical currents induced in the liquid, they are closed, no electrodes are present, there is no electrolysis, and there is no polarization.

The preliminary experiments, performed with the apparatus described in our last paper, clearly showed that with suitable means a measurable and even a large effect might be produced. Accordingly the experiments were continued with the very powerful and delicate apparatus shown in Plate VIII. One litre of liquid is put into the vessel A, which consists of a glass shade, the open end of which has been roughened with emery, and a strip of strong brown paper attached to it with paste. Two vertical strips of ebonite are fastened to the paper ring with shellac, and bound round with cotton, and the whole well varnished with shellac varnish. These strips are fastened by ivory pins to the boxwood beam B; and to the centre of this beam the torsion wire w is made fast by being wound three times round the little reel r and the end secured by a needle-point. The torsion wire passes over a zinc wheel

* Read on June 26th.

† Proceedings of the Physical Society of London, vol. iii. part iii. p. 127; Phil. Mag. December 1879, vol. viii. p. 449.

about 13 feet above the beam B, and down again to the same level, where it passes round the zinc screw z; so that by turning this screw the vessel A can always be brought to the same level, whatever be the specific gravity of the liquid within it. To the top of this vessel are attached two glass arms, one on each side, one carrying a photographically-reduced scale, s, on glass, and the other a counterpoise. The vessel A is entirely enclosed in a screen shown dark in the Plate. The thick portions of the screen are of wood; but the thin cylindrical part immediately round A is of thin ebonite, and the hemispherical part below A is of glass. This screen prevents the whirlwind of air caused by the revolving magnets from interfering with the motion of the vessel A. It also supports a microscope, H, provided with cross-wires, which is used to read the position of the scale S. The magnet consists of 24 semicircular bars put together as shown, so as to form a ring, the similar poles of the different bars being kept from touching one another by the fourteen pieces of iron shown dark in the plan. The magnet is $7\frac{1}{2}$ in. in external diameter, and weighs about 18 lbs. The magnetic field within it is remarkably uniform; iron-filings on glass take the form shown by the streak lines in the plan. The magnets are attached by four brass plates to the gun-metal wheel, G, which screws against an accurately turned shoulder on the vertical steel shaft, I. This shaft runs in cylindrical split gun-metal bearings; but its weight is taken by a slightly convex hardened steel round-headed pin let into the shaft and resting on a plate of quartz. The framework which carries the bearings consists of five triangles of cast iron screwed together in the form of a distorted octahedron, a form which gives great rigidity; it is omitted in the Plate to avoid complication; but its general outline is shown by dotted lines s. The lower triangle of the framework is screwed to a thick slab of mahogany, which is clamped to the stone mantlepiece of the room; and one hundredweight of iron stands on the wood to increase its inertia and make the whole thing more steady. Near the top of the shaft I a fine screw is cut, which gears with the worm-wheel m of 100 teeth. This wheel has also cut on its edge a screw of the same pitch as that on the shaft I; so that its edge is divided into a series of square pyramids, and it gears

as a screw into the worm-wheel n of 100 teeth : n therefore turns round once for 100 turns of m or for 10,000 turns of I. At every turn m makes an electric contact and sounds a bell; n has its face divided and numbered. Therefore by observing occasionally the exact instant at which the bell sounds, and then the reading on n, a continuous record of the speed can be kept, at the same time that s is being observed with the microscope. A pulley-wheel on I is connected by a catgut band with a small steam-engine driven by steam from the boiler which supplies the building. The steam-pressure varies so much that the resulting changes in speed in the engine have caused the greatest inconvenience, sometimes a whole day being lost. Some form of absolute governor will have to be devised in order to avoid great loss of time.

On the lower side of the beam B is a small glass hook, from which may be hung a disk of brass D, the use of which will be explained below. The dimensions of most of the parts of the apparatus may be found from the Plate, which is drawn to the scale of almost exactly $\frac{1}{4}$. The torsion-thread is of hard drawn steel wire about 13 feet long and 0·007 in. in diameter. The space in which the cylindrical part of the screen is placed between the poles of the magnet and the outside of the cell is only about $\frac{3}{16}$ in. wide, so as to get the greatest possible effect from the magnets. When the machine was put together the magnets were found to be slightly out of balance; so a plate of brass full of tapped holes was fixed to the light side, insufficient in weight to restore the balance, and then small screws of brass were screwed into the holes until the balance was perfect. By this means the magnets were made to run so smoothly that at 3000 turns a minute scarcely any tremor could be felt; but always on passing a certain critical speed (about 1300 turns a minute), at which the period of vibration of the whole machine and mantlepiece was probably equal to the time of rotation of the magnets, the machine set up a vibration, gentle at first, but increasing with the speed, which seemed at first as if high speeds could never be attained. But it was found that if, as soon as this effect took place, one of the screws of the upper bearing was loosened the oscillation ceased suddenly, and then the screw could be tightened again, and the speed increased to any extent without the

slightest sign of vibration reoccuring. In fact the magnets spun like a great top, though the screwed-up bearing permitted no shake of the shaft within it. On passing the critical speed when stopping, the oscillation set up is hardly noticeable.

Before beginning the experiments it was necessary to determine what effect, if any, the magnets had on the vessel A. For this purpose it was filled with distilled water, and the magnets made to run at speeds high and low; but not the slightest movement of the scale could be detected by the microscope so long as the magnets were revolving. Had it moved the hundredth part of a millimetre, that must have been seen; but when the magnets were stopped the scale was found to have moved; and as the magnets were turned round to successive positions through 360°, the scale went through a complete oscillation of 18 divisions. These two preliminary experiments showed that, though the cell was affected by placing the magnet in different positions (an effect probably due to the three turns of the torsion-wire round the reel in the beam having a directive action), yet electrically the cell was all that could be desired, and any torsion observed during the rapid revolution of the magnets must be due to the conductivity of the liquid in the cell. No currents could be induced in the torsion-wire round the reel, for they formed an open circuit; but even if closed, the reaction of the induced currents on the magnets would be inappreciable, owing to the small diameter of the coil and its great distance above the magnets. It is also clear that the magnets could have no mechanical action on the cell due to air-currents, vibration, &c. It should be mentioned here that the screen was fixed to a panel screwed to the wall, so as to be quite independent of any thing connected with the magnets; also the torsion-wire was hung from a bracket fixed to the wall under the cornice of the room. This separation of the supports of the various parts is to ensure there being no mechanical action causing torsion due to vibration &c., an effect observed by Snow Harris in certain of his experiments.

Having now made clear the construction of the apparatus, it will be well to explain next the principle of its action, and then to describe the method of working with it, giving at the same time the few results that have been obtained so far.

When a conductor is in a moving magnetic field it is urged in the direction of motion by a force which varies directly as the relative movement, directly as the intensity of the field, and directly as the conductivity of the conductor, *i. e.* if the form of the conductor is always the same. In the present case the form of the conductor is necessarily always the same, and its situation in the magnet is so too; for its height is adjusted by the screw *z* till a horizontal line on the scale *s* is seen on the cross-wires in the microscope. The strength of the magnet is nearly constant; and its variations are allowed for by a method which will be described below: the speed of the magnets can be accurately measured by the counter; and therefore the torsion of the wire *w* gives an exact comparative measure of the conductivity of the liquid in the vessel A, provided that the torsion of the wire is uniform and that the movement of the liquid in the cell has no influence on the result. As the wire used cannot be made to carry 7 lbs., but has in the course of the experiments to support the cell together with a litre of liquid of any specific gravity between those of water and oil of vitriol, its torsion is any thing but constant from day to day; but its variations, due to these great changes in the load and to slight changes in temperature, are accurately allowed for at the same time that the change in the strength of the magnet is taken into account; and therefore, if movement of liquid in the cell does not vitiate the results, this method of comparing the conductivity of electrolytes is free from error.

To ascertain what effect movement of liquid in the cell has on the result, it will be necessary to examine more closely how the torsion of the wire is produced. When the magnets are revolving, currents are induced in the liquid in a direction to oppose the motion; so the liquid is pushed round in the direction in which the magnets are revolving by a force which is directly proportional to the difference in speed between the liquid and the magnets. If there were no friction of any kind tending to resist the motion of the liquid, it would in time attain a velocity equal to that of the magnets; for so long as it was revolving more slowly than the magnets there would be a force urging it on. But there is friction between the outer layer of the liquid and the vessel, and between each successive cylindrical layer and the one outside it; and

therefore the liquid never attains any great velocity at all. But each elementary cylindrical layer soon reaches that speed at which the force urging it forward is equal to the friction between it and the layer outside; and therefore the torsion measured is exactly the same that would be obtained if it were possible to integrate the force from the centre to the edge of the vessel. If this reasoning is correct, the liquid should be revolving fastest at the centre and more slowly outside; and this has been proved to be the case by a very striking experiment. A solution of indigo was made of such a specific gravity that a drop of it would just sink in the liquid used; and when the magnets were revolving at a great speed a series of drops were delivered at different distances from the centre. They all fell in spiral lines, each one revolving more quickly than the one outside it. Then, on reversing the engine and repeating the experiment the spirals were found to be going the other way, but, in each case, in the same direction as the magnets. The average speed of the liquid (30 p. c. H_2SO_4, 70 p. c. H_2O) was about one turn in ten minutes. It is now possible to see to what extent movement of liquid in the cell affects the result. As soon as the rotation of the liquid has become constant, the force urging it forward is equal to that due to friction retarding it; the torsion of the wire therefore is an exact measure of the force on the *moving* liquid. But the force is directly proportional to the relative speed, and not to the actual speed, of the magnets; and we have seen that the liquid does not revolve more than once for 20,000 turns of the magnets; and therefore the error made on the supposition that the liquid is at rest is not more than the 20,000th part of the whole result—a quantity altogether inappreciable, for neither the speed nor the torsion can be measured with such accuracy.

The apparatus described was finished and the experiments begun on April 5, 1880; but it was immediately found that the behaviour of the wire was such that no results of any value could be obtained; for the zero on the scale (that is, the position without torsion) was constantly changing, so much so that sometimes without any apparent cause the scale would move ten divisions in a few hours. As 11·4 divisions correspond to an angular movement of one degree, and as the greatest torsion ever observed caused a movement of only 45

divisions, it seemed that some other wire would have to be used. But, again, steel was the only metal that could be used, as a weaker metal must have been much thicker, and the torsion of a thicker wire would have been too great. Weights were hung on the wire and twisted several times round and then left, to see if the wire would improve by such treatment, but without effect. Then some other wire was sent for, and the machine left for six weeks. During this time the old wire became a little rusty; and when the experiments were to have been continued with the new wire, the old wire was tried once more and was found greatly improved, possibly from the removal of the hard skin by rust. During the course of one experiment, lasting over an hour, the zero had not shifted the tenth part of a division. The next day the same acid was examined again; and the two results differed by only 1·3 p. c. This result seemed very satisfactory, especially as possible changes in the strength of the magnet or in the torsion of the wire were not considered; and therefore we determined that the experiments should be continued with the old wire. So it was well rubbed with sperm oil to stop the rust from increasing in quantity and destroying the wire.

The method of carrying out the experiments must be described next. It has already been shown that the magnets when at rest have a directive action on the cell, but when in motion their action on the cell itself is nothing; yet if a conducting liquid is in it the cell is turned round. Also the zero of the scale can only be determined after the liquid is put in; and therefore there is no possibility of observing the zero directly. But as the torsional effect is proportional to the speed, by running the magnets first at a low and then at a high speed and taking the difference in the speeds (S) and also the difference in the readings (T), and dividing S by T, a number is obtained which is a measure of the resistance of the liquid in the cell. To diminish as much as possible all chances of error, every liquid was examined at four speeds—two with the magnets turning in one direction (+), and two in the other direction (−); and the results were taken in pairs, in the order of observation, to avoid errors due to such slow changes in the zero as were still liable to take place. If the strength of the magnets and the torsion of the wire were both

constant, nothing more would be required; but as both are liable to change, some standard of comparison by which the value of an observed deflection can be measured is necessary. The most obvious plan is occasionally to examine some given liquid of good conductivity, *e. g.* 30 p. c. sulphuric acid, and consider variations in the result due to changes in the machine, and correct the measures obtained for other liquids accordingly. But this plan would involve a great waste of time, as from two to three hours are required for the examination of a liquid; and it would not be trustworthy, for it cannot be supposed that the torsion of a wire is the same when stretched to 50 p. c. and to 80 p. c. of its breaking strain; and therefore the standard of comparison must be applied at every experiment when the liquid under observation is in the cell. Accordingly a disk of thin sheet brass, D, three inches in diameter, was used as a comparison plate. It is hung to the glass hook below the beam B, immediately after the observation at the fourth speed has been made, without stopping the engine or touching any other part of the apparatus, and the increase in torsion noted. This increase in the torsion when corrected for speed should be constant; and the slight variations in the increase are due to changes in the magnets, or the wire, or both, the effect of which may therefore be allowed for accurately. It is true that possible changes in the distribution of the magnetism cannot be taken in to account; so that, if the upper magnets changed more or less than the lower ones, the comparison plate would indicate too great or too small a change; but no error of any importance is likely to result from such a cause. Also changes in the conductivity of the brass due to temperature have not been considered, though they can be at any time. After the observed conductivity of a liquid has been corrected by means of this comparison plate, it is independent of changes in the magnets or the wire, and so all results obtained during any length of time are directly comparable. Of course, after any great length of time an experiment would be made on 30-p.-c. sulphuric acid to serve merely as a check. There is one more point that must be noticed before giving the results. Owing to the high specific gravity of sulphuric acid, it seemed hardly safe to use the full quantity of 1000 c. c. of acids stronger than 60 p. c.; and therefore the smaller quantity of 750 c. c.

was used; and in order to compare the effect produced by 750 c. c. with that by 1000 c. c., 750 c. c. of 35-p.-c. acid was taken, and its effect observed after correction by the comparison plate. The apparent resistance obtained was 1·66 times the true resistance given by 1000 c. c.; and therefore, of the four solutions containing respectively 70, 80, 90, and 95·5 p. c. anhydrous sulphuric acid (H_2SO_4), only 750 c. c. were taken, and the observed resistance divided by 1·66.

The method of calculating the results is given next. The speed is measured by the number of turns in one second. Each of these numbers, together with the reading of the scale

H_2SO_4 25; H_2O 75. T. 16° C.					
Exp.	*a*.	*b*.	*c*.	*d*.	*e*.
Speed	−16·81	−34·60	+31·59	+14·68	+14·04
Reading	108·7	88·1	165·3	145·8	174·3

in the line below, is the result of at least four observations. *e* is taken with the comparison plate attached. The first four columns are then taken in pairs, and the sum or the difference of the two speeds taken, according as they are of unlike or of like sign, and put in the first column of the next table; then the differences in the readings are taken and put in the second column.

	Speed.	Torsion.	Zero.	$\frac{\text{Speed}}{\text{Torsion}}$.	
a and *b*	17·79	20·6	128·2	·864	·860
b and *c*	66·19	77·2	128·4	·857	
c and *d*	16·91	19·5	128·9	·867	
e.....	14·04	45·6	128·7	·4795	
		16·3			
		29·3			

$\frac{\cdot 860}{\cdot 4795} = 1{\cdot}794$, the corrected resistance of the liquid;
55·80, the corrected conductivity.

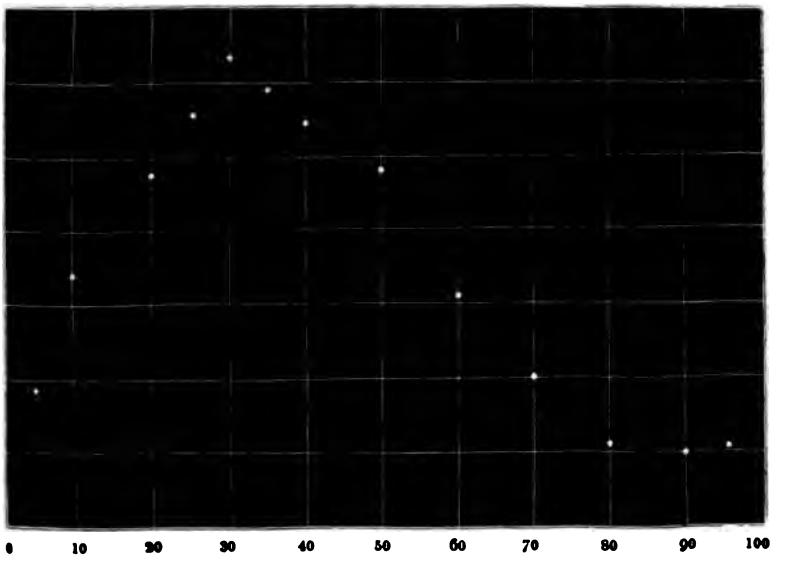
The zero in the next column is obtained from the two observations by a simple proportion sum; and the numbers in the last column are obtained as shown, and are a measure of the resistance of the liquid, but uncorrected by the comparison plate. The three figures obtained differ; but the greatest weight is given to the observation at the highest speed, and ·860 is taken as a fair mean. To make use of the observation *e*, the probable zero must be found by examining the numbers already obtained. As they indicate a gradual rise in its position, a number higher than the mean is taken. This shifting in the zero caused more uncertainty than any thing else; and it is this that limits the accuracy of the investigation. The probable zero subtracted from the reading 174·3 gives the torsion 45·6, due to the liquid and to the plate together; but the torsion due to the liquid alone, of the apparent resistance ·860 already found, and with the speed 14·04, is 16·3; and this, subtracted from 45·6, leaves 29·3, the torsion due to the plate alone; and this divided into the speed 14·04 gives the quotient ·4795, an arbitrary number, the changes in which from time to time represent changes in the magnets or wire. From this the corrected resistance 1·794 is found as shown; and its reciprocal is the conductivity. All these numbers are in themselves entirely arbitrary; but they are all comparable with one another; so that any number of liquids may have their conductivities compared with one another, and eventually with that of some standard metal.

The conductivities of sulphuric acid and of sulphate of copper, the only liquids examined at present, are given in the following Table. The conductivity-curve of sulphuric acid agrees in every important particular with Kohlrausch's, which was obtained with alternating currents, the chief difference being rather a sharper rise to and fall from the first maximum; otherwise the position of the two maxima, of the minimum, and of the point of contrary flexure agree most perfectly*. The experiments will be continued on other liquids.

* A large quantity of oil of vitriol was boiled in platinum capsules, cooled, and thoroughly mixed. 3·7496 grams gave 8·5114 grams Ba_2SO_4, showing 95·5 per cent. of H_2SO_4. After dilution to obtain the requisite strengths, the clear acids were siphoned off from the deposited sulphate of lead.

Per cent.*	Conductivity of					
	H_2SO_4.		T.	$CuSO_4$.		T.
			°C			°C.
5	18·53	...	19	1·62	...	17
10	34·10	...	17	2·56	...	17
15	.....	...	...	3·58	...	17·5
17	.....	...	...	4·47	...	19
20	47·72	...	17			
25	55·80	...	16			
30	63·22	...	16			
35	58·99	...	15			
40	54·01	...	15·5			
50	48·23	...	16			
60	31·26	...	16·5			
70	20·34	...	16			
80	11·61	...	16·3			
90	10·06	...	18			
95·5	10·74	...	18			

* *Conductivity of Sulphuric Acid and Water.*
Abscissæ are percentages of H_2SO_4. *Ordinates* are conductivities.



PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

JANUARY 1881.

XII. *Air-Thermometers.* *By* D. WINSTANLEY*.

[Plate V.]

A THERMOMETER which makes its indications in consequence of the dilatation and contraction of a gas offers several advantages over one which depends therefore on the volumetric variations of a liquid. Gases under constant pressure expand considerably more than liquids do for the same elevation in their temperature. Hence an air- or gas-thermometer, having the same size of bulb and tube as one in which a liquid only is employed, will have a more legible and open scale. Again, a given volume of a gas at the ordinary barometric tension of the air upon the level of the sea, when compared with an equal volume of a liquid body, requires so utterly insignificant an amount of heat to elevate its temperature through a given range, that a gas-thermometer is enormously more sensitive than one which depends upon a liquid for its expansional effects. And, finally, the very equal manner in which gases are dilated under the influence of equal increments of heat is a very strong point in favour of an air-thermometer.

As constructed by Galileo, the air-thermometer unfortunately gave readings which were influenced by the barometric

* Read June 26th, 1880.

variations of the outer air, a circumstance which has limited considerably its use and application. Happily it is not difficult to construct an instrument which shall be free from this defect. If we take an ordinary mercurial barometer made after a certain well-known pattern, *i. e.* with a bulb-shaped cistern surmounted by a neck into which we may insert a cork, and if as a matter of fact we *do* insert a cork, obviously that barometer ceases to show the tension of the outer air, and is a barometer only to the air enclosed within its bulbous cistern. But as the tension of this air will vary with its temperature, the height of the mercurial column will vary therewith as well; and that which *was* a barometer will, by the mere insertion of a cork, have become an air-thermometer, the readings of which are uninfluenced by the barometric variations of the external air. There is, of course, no reason why the tube of such an instrument should be so little or so much as thirty odd inches long. Neither is it necessary that mercury should be the liquid used. Sulphuric acid, for instance, will answer just as well. It is not even needful that the liquid should be non-volatile at the temperatures to which the apparatus is exposed. The objection which exists to the employment of a volatile liquid in the ordinary barometric column does not here apply; for that depression which the vapour tends to produce in one limb it tends to produce in the other one as well, and so leaves the equilibrium of the liquid undisturbed, and dependent only on the expansion and contraction of the air. It is merely needful, then, in this form of air-thermometer, that the gas enclosed shall be submitted to the definite pressure of an isolated barometric column; and we may employ what liquid and what length of tube we please. We may even construct a veritable air-thermometer *without* a barometric column by resorting to some other means of obtaining the definite pressure we require; and to this end the author has employed a vacuous corrugated elastic box similar to those contained in aneroid barometers; but he has used it with the spring inside. This thermometer is shown in fig. 1. At the bottom we have a rigid box with the elastic one enclosed. The rigid one is sealed; and the elastic one is surrounded by a liquid which rises some distance up a tube, in which the indications will be made. The tube is sur-

mounted by a bulb of air. This air, with a rise of temperature, expands and forces down the substance of the liquid column into the space made for it by the compression of the elastic box; and with a fall of temperature the reverse of course takes place.

The air-thermometer which I first described (that with the isolated barometric column) cannot, in the shape in which I have described it, be regarded as having a convenient form, inasmuch as through the greater portion of its length the liquid will never move. Obviously the index of the barometric column will not reach the level of the liquid in the cistern until the rational zero is attained; and the amount of space which marks the range between the freezing- and the boiling-points of water will have nearly three times as large a space below, devoted for the greater part to readings which will very likely never be observed.

I find, however, a very convenient instrument may be produced if, in its construction, two liquids are employed, as shown in fig. 2. There we have a mercurial barometric column. Its cistern is connected with the bulb of air by a long and upright tube. A column of sulphuric acid rests upon the mercury within; and the summit of the barometric tube is considerably enlarged. The tube connecting the barometer-cistern with the bulb of air is comparatively narrow in its bore. In consequence of this arrangement, the vertical amount of liquid motion is practically confined to the substance of the lighter column, and is several times greater in extent than if one liquid only had been used. We are accordingly enabled in this way to make an air-thermometer, of which the index shall move over pretty nearly its total length for such natural changes in temperature as we meet with in a given place. Such an instrument was constructed for me in Paris in 1878. It has hung in the Loan Collection of scientific instruments at South Kensington Museum for something like a year; and the accuracy of its indications does not seem impaired. The desirability of using coloured sulphuric acid as the material of the lighter column will very likely be a matter for dispute. I am aware that other experimentalists who have employed it in barometers have found a depression of the column has ensued and a crystalline deposit been left on the mercurial

surface. It is for me, however, to speak as I have found. Twelve months ago my instrument, when laid down flat, had a bubble of air in the mercurial limb purposely introduced, and of obviously less volume than a small pin's head. The instrument has never been reversed to float it out, and the volume of this air is still capable of the same description as before. This thermometer is four feet or more in length; and the diameter of its index-column (which is cylindrical) is the tenth of an inch or so. Its Fahrenheit degrees are represented by spaces of the third part of an inch; and it attains an exceedingly close approximation to the actual temperature of the air in some few seconds' time; whilst an alcohol thermometer, moving an equal column through equal spaces for equal numbers of degrees, and with a bulb similar in shape but proportional in size, requires some hours to reach an equally close approximation to the temperature of the air.

The air-thermometers I have now described have depended for their indications on the movements of a liquid in a tube. I have, however, devised another, in which the movement of the tube about the liquid is the method I employ. In this thermometer (fig. 3) the barometric tube is circularly curved and mounted concentrically upon a wheel of brass, which is supported in a vertical position by a knife-edge of hardened steel which passes through its geometric centre and rests on agate planes. Adjustments are provided by means of which the centre of gravity of this arrangement can be raised or lowered; and the mercurial column which is seen extending on the right is balanced by a weight, which is seen depending on the left. The whole is surmounted by the bulb of air; and the vacant space above the mercury upon the right is the Torricellian vacuum of the barometric column. Changes in temperature are shown by this thermometer in the varying angular positions of a needle, prolonged from one or other of the radii of the wheel, and counterpoised by a piece of metal on the other side. When the centre of gravity of this system has been made coincident with the point on which it turns, the liquid, under changes of temperature, is almost absolutely motionless, whilst the tube which holds it moves. By bringing the extremity of the needle into contact with a cylinder driven by clockwork at an even speed, we have a thermograph

complete. Of course some delicate method of recording must be used; and I have hitherto employed the smoked-paper process, so much adopted in the observatories of France. I prefer to make my records on the albumenized paper prepared for photographic use, and, for the sake of the beauty of the black, to smoke it over the flame of a common tallow dip. I then fix the records by immersing, cylinder and all, in lac varnish diluted with methylated spirit. In this process there is not the slightest danger of injuring the results; and these, when several times revarnished and mounted upon card and rolled, are doubtless permanent, and are certainly incomparably more beautiful than any other tracings I have seen.

XIII. *On Action at a Distance.* *By* WALTER R. BROWNE, *M.A., M. Inst. C. E., late Fellow of Trinity College, Cambridge.**

THE object of this paper is partly historical, partly critical. In discussing what is called "Action at a Distance," the statement is frequently made that Newton was of opinion that "nobody who possessed a competent faculty of thinking" could possibly imagine such a thing to exist. The writer wishes, first, to show historically that this is by no means an accurate representation of Newton's views, and, secondly, to consider critically whether the repudiation of "action at a distance," which is now certainly common, is, after all, justified by the facts of the universe.

In the first place, Newton's words, contained in the Third Letter to Bentley, are as follows:—"That gravity should be innate, inherent, and essential to matter, so that one body may act on another body at a distance through a vacuum, without the mediation of any thing else by and through which their action and force may be conveyed from one to the other, is to me so great an absurdity that I believe no man who has in philosophical matters a competent faculty of thinking can ever fall into it. Gravity must be caused by an agent acting constantly according to fixed laws; but whether this agent be

* Read November 13, 1880.

material or immaterial I have left to the consideration of my readers."

Now, in speaking of this passage, it is usual to quote the first of these sentences only, and omit the second; and yet it is obvious that the second is intended to explain and define the sense of the first. Read by the light of the second, it seems perfectly clear that all which is denied in the first is the possibility of gravity being an inherent property of matter, in the sense in which hardness, inertia, &c. may be considered as properties. What Newton might seem to have had in his mind was the coarse materialism of Democritus and Lucretius, which held that all the phenomena of the universe were due to the mere motions and clashings of its ponderable atoms. This at least, he would hold, was disproved by his discoveries, because to defend it by assuming an occult property of matter, which could extend to a distance, was absurd. All, however, which he really says is that one body cannot, *uncaused*, act on another at a distance. In the second sentence he expressly uses, not indeed the word Cause, but the much stronger word Agent; and he distinctly contemplates the possibility of this agent being, not material, but immaterial. It seems clear, therefore, that he is thinking of nothing less than of denying that action at a distance may, as a matter of fact, exist. Indeed, when we consider that this passage occurs, not in a mathematical work, but in a letter expressly treating of the relation between the discoveries of science and the doctrines of theology, and when we remember the strong theological views which he is known to have held, it seems impossible to doubt that he would have been perfectly contented to acquiesce in the immaterial nature of the agent of gravity; though, no doubt, he would have been perfectly open to consider any reasonable hypothesis of a material agent which might have been placed before him.

Having thus attempted to restore the true sense of this famous passage, the writer will go on to consider, in the second place, how far the conception of Action at a distance actually merits the condemnation it has received. It seems desirable to commence with a definition, and to lay down the consequences which flow from it in general, before proceeding to consider particular cases.

Definition.—"By the term 'Action at a distance' is meant that direct action takes place between two bodies, separated from each other by a finite distance, without the intervention of any other body whatever."

Now if action at a distance does not exist, then the only *direct* way in which one body (A) can act upon another (B) is by coming into absolute contact with it; and the only *indirect* ways in which it can act upon it are two, viz. either by projecting a third body from contact with itself into contact with B, or by diverting some third body which, if not diverted, would have come into contact with B.

If action at a distance does not exist, all the actions between all the bodies of the universe must be explicable, by impact, on one of these three hypotheses. If any phenomenon takes place which cannot be so explained, then action at a distance does exist. It may be added that, if it is shown to exist in any one instance and at any distance, there is no probability against its existence in any other instance and at any other distance. It is no less wonderful, and no more wonderful, that two bodies should act on each other across the hundred millionth of an inch, than that they should act on each other across a hundred million of miles. In fact it is easy to conceive a creature so large, or so small, that the difference between these two distances would appear to it quite insignificant.

Let us now take the above three hypotheses and see whether all the actions in the universe can be explained by them.

First, as to the direct impact of one interacting body A upon another B. This may no doubt explain certain obvious cases, as the stoppage of a falling body when it reaches the earth; but it is equally obvious that there are many others, such as gravity, magnetism, &c., which it cannot explain. In fact, it will be granted that in these and many other cases there is an *apparent* action between bodies at a distance; and our business is to see whether it is real or apparent only.

Secondly, with reference to the projection of other bodies from A against B. It is clear that the actions thus produced can be actions of *repulsion* only: therefore this principle cannot explain any case of attraction. Moreover the power by which A is able to project these bodies against B itself requires explanation. If they have previously been at rest in

relation to A, then A can only project them by some innate explosive power totally different from impact. And if any one suggests that the bodies have previously been in motion with respect to A, and that they are projected by elastic reaction from A, then he must be asked to give an explanation of elasticity from impact only, and without introducing action at a distance. In any case it seems clear that this principle will not carry us very far in explaining the actions of the universe.

Thirdly, we have the principle that A may stop certain other bodies, which would otherwise have impinged upon B. This principle, as is well known, was applied by Le Sage to explain the facts of gravitation *. His hypothesis was that showers of "extramundane particles" are sweeping through space equally in all directions, and that a fraction of these, being intercepted by A and B, urge those two bodies towards each other. This hypothesis is encumbered with a large number of arbitrary assumptions; and the latest supporter of the theory, Mr. S. Tolver Preston†, presents it under a greatly modified form. He supposes the solar system to be immersed in an impalpable gas, the particles of which have a mean length of free path greater than the distance through which gravity has been observed to hold (greater, therefore, than the distance between the Sun and Neptune), and which tend to bring together, by the resultant of their impacts upon them, any two bodies within that range. It is not proposed in this paper to attempt an exhaustive discussion of this theory; but were it left as an unquestioned explanation of gravitation, it might be thought a strong presumption that all other actions were to be explained on the same principle. It may therefore be remarked that it is encumbered by very serious difficulties. In addition to those put forward by Dr. Croll and others, the following may be suggested:—

(1) Mr. Tolver Preston founds his theory on the late Prof. Maxwell's proof ‡, that "a self-acting adjustment goes on among a system of bodies or particles in free collision, such that the particles are caused to move equally in all directions,

* Sir W. Thomson, Phil. Mag. May 1873.

† Phil. Mag. Sept. 1877, Nov. 1877, Jan. 1878.

‡ S. Tolver Preston, Phil. Mag. Sept. 1877.

this being the condition requisite to produce equilibrium of pressure" *. Now this equilibrium of pressure, and the theory based upon it, may be perfectly true for all known gases. But all such gases are under certain conditions, which need not hold universally; in especial they are *bounded* in some way. The atmosphere, which is the freest gas we can observe directly, is bounded by the earth on one side and space on the other, and is prevented from passing into space by the action of gravity. But we have no right whatever to assume such a boundary for interstellar space, or to assume that a gas filling such a space would have equilibrium of pressure. The probability would seem to be the other way; for any disturbance in such a gas would tend to propagate itself in all directions for ever. In any case, Maxwell's results must be proved, not assumed, to hold for this gravity-gas, as it may be termed.

(2) Another difficulty in the theory is the enormous degree of porosity which it postulates for solid bodies. To fix our ideas, suppose that, in any unit of surface of a solid, one millionth part only is occupied by the really solid part (*i. e.* the part which would stop the particles of the gravity-gas) of the molecules composing that surface. Then it is obvious that a layer of such molecules a few millions thick would be practically certain to stop the whole of the gravity-particles impinging upon it. No arrangement of the molecules one behind the other will get over this, because the gravity-particles are assumed to come in all directions at once. Now such a layer would certainly be no more than a small fraction of an inch in thickness. And yet it is absolutely necessary for the theory (in order to explain how gravity varies as mass) to suppose that these gravity-particles pass through the 16,000 miles of the earth's diameter, under the enormous density, pressure, and temperature which must exist in the interior, without having more than a very small proportion of their number stopped in the passage. The difficulty is rendered the greater when we remember that, *ex hyp.*, these attenuated molecules cannot act on each other at a distance, in producing the various

* I have, unfortunately, failed to verify the reference to this paper of Prof. Maxwell's, given by Mr. Tolver Preston, and therefore can speak of it only from his description.

phenomena of solid bodies, but only in one of the three modes of direct impact enumerated above.

(3) Another difficulty arises from the fact that the heavenly bodies are not found to experience any perceptible resistance whatever in passing through this gravity-gas. It is clear that if a body be in motion in the midst of a shower of such particles coming equally from all directions, it will receive a greater number of blows on its front surface, and a less number on its rear surface, than if it were at rest; and consequently its motion will be retarded. The only way of surmounting this difficulty is to suppose that the heavenly bodies, in relation to the gravity-gas, are practically at rest; in other words, that the velocity of the gravity-particles is practically indefinite compared with that of the heavenly bodies. Since in the case of Mercury, for instance, this latter velocity is about thirty miles per second, it is clear that the velocity of the gravity-particles must be something altogether beyond calculation; and then, since the effect of the collisions is, after all, very limited, the mass of the particles must be assumed correspondingly small. Hence our conception of the gravity-gas must practically be that of an indefinite number of indefinitely small particles moving in all directions with indefinitely high velocities—a conception from which it hardly seems safe to draw any definite conclusion whatever.

(4) The last-mentioned difficulty leads to another, viz. to fix the relations between the gravity-gas and the luminiferous æther. They cannot be the same; for Mr. Tolver Preston and Prof. Maxwell have shown * that the velocity of propagation of a wave in such a gas $=\frac{\sqrt{5}}{3}\times$ the velocity of the gas-particles. Since the velocity of waves in the æther is about 180,000 miles per second, this would give the velocity of the particles themselves = about 130,000 miles per second—a velocity immensely below what is required to account for the fact of non-resistance. But if the æther and the gravity-gas be different bodies, the particles of the latter must be colliding continually with those of the former, as they collide with the molecules of ordinary matter. How is it that no effects due

* S. Tolver Preston, Phil. Mag. June 1877.

to such collisions are observed? It would seem likely that they would assume the shape of a diffused glow of light and heat, growing more and more intense as the translatory motion of the gravity-particles was turned into vibratory motion of the æther-particles. It is needless to say that nothing in the least resembling this takes place.

We will here leave the discussion of Le Sage's impact theory, as explaining the particular case of gravitation, and go on to inquire how the same, or any other impact theory, can explain some other phenomena of the universe. We will first take those of cohesion.

Cohesion.—To fix our ideas, let us take the case of a square bar of good wrought iron or mild steel, 1 foot long and 1 square inch in area. Then the following two facts, amongst others, have to be accounted for:—

(*a*) The extension of the bar as a whole (and therefore the extension of the mean distance between the successive layers of its molecules) by $\frac{1}{1000}$ of its length is sufficient to produce between the successive sections of the bar a stress of tension (taking the form of an attraction between the sections) of about 15 tons, say 8000 times the attraction exercised by the earth upon the whole bar when placed in contact with it.

(*b*) The contraction of the bar through the same relative distance is sufficient to produce between the sections a stress of compression (taking the form of a repulsion between the sections) also of 15 tons or thereabouts.

Can these two facts be explained on any of the three impact theories, which we have shown to be the only possible ones? It seems almost sufficient to ask the question; but it may be well to take them in order.

(1) Can the facts be explained on the hypothesis of direct contact between the molecules? Were this true, it would be impossible to produce any contraction of the bar without forcing two solid bodies into the same space. It is obvious that it will not do to suggest that the contraction may be in the molecules themselves; for then we have only to transfer the inquiry to the particles composing those molecules. Are these particles themselves in contact or not? If they are not, they cannot keep the bar together; if they are, they cannot be compressed. Again, if the molecules are spherical, or of any

other regular shape whatever, they cannot oppose any resistance to separation, *i. e.* there can be no tensional stress. The only way out of this seems to be to conceive them shaped something like burrs, and holding on to each other by hooks. This is altogether contrary to the vortex-atom and all other known theories of molecules. Moreover such burr-like molecules must hold to each other somewhat loosely; and a certain amount of extension would be necessary (as in the case of a slack chain) before any resistance was experienced. But no such slackness has been observed with the most delicate instruments; and we have seen that an extension of $\frac{1}{1000}$ is sufficient to produce an enormous resistance. For these and the like reasons the hypothesis of direct contact is inadmissible.

(2) Can the facts be explained on the hypothesis of particles projected from the molecules of one section against those of the next? Now it is clear that any effect due to this cause will be merely an effect of repulsion. Consequently the end section of the bar will be repelled from that next to it, and will fly off; another body brought into contact with the bar will be repelled by it, &c. For these and the like reasons this hypothesis is inadmissible.

(3) Can the facts be explained on the same hypothesis as that of Le Sage, viz. of independent particles flying through space and intercepted by the molecules of the bar? In the first place, it is clear that these cannot be the particles of the gravity-gas; for if these pass through the earth without having more than a small proportion stopped, it is clear that the number intercepted by an inch of iron will be infinitesimal. We should have to conceive, therefore, a separate atmosphere for each solid body, and an atmosphere the effects of which are many thousand times as great as that of the gravity-gas. But, further, let us assume this atmosphere, and consider what will happen when the bar is extended. Any one section will be removed to a greater distance from the next, and its sheltering influence will be diminished in the inverse ratio of the squares of the distances. Consequently the effect of extension will be to diminish the attraction between the sections; whereas the actual effect is enormously to increase it. For these and the like reasons this third and last hypothesis is also inadmissible.

The two latter hypotheses, and any combination of them, labour under a further and fatal disadvantage, viz. that the cohesion of the bar would be different in different parts. Thus in whatever way the flying particles are supposed to move, it is evident by symmetry that the central section will be solicited in one direction precisely as much as in another; hence the slightest pull will cause the bar to part in the middle.

The above trains of reasoning are not long, and rest on undoubted facts; and the writer has not been able to discover any flaw in them. But unless some such flaw, and a fatal one, be discovered, it must be held to be demonstrated that the phenomena of cohesion cannot be explained except on the hypothesis of action at a distance.

Magnetism.—Of the many difficult cases presented by the phenomena of electricity, it will be sufficient to cite one of the simplest. When an ordinary iron magnet is brought near a piece of iron, the latter is attracted to it. Now the first impact hypothesis is here inadmissible, because the bodies are not in contact; and the second, because the effect is one of attraction, not of repulsion. Thus the only possible explanation of this fact, apart from action at a distance, is by supposing that the magnet intercepts a proportion of a shower of particles which would otherwise impinge equally in all directions upon the iron. It is of course possible to imagine a "magnetism-gas," different again from both the "gravity-gas" and the "cohesion-gases," to which this would apply; but the writer has not been able to imagine any property, consistent with the principle of impact, which could be given to the magnet, such as to make it intercept these particles, when the same magnet, before being magnetized, would be unable to do so—and also such as would make it intercept the particles flying towards a piece of iron, and not to intercept the particles flying towards a similar piece of brass.

Vibrations.—Any thing like the vibration of a molecule about a central position (which is the fundamental idea in explaining Heat, Light, and all undulatory movements) seems to be impossible on this theory. For a molecule, once started, is in the position of a free projectile through space, and will continue to move in a straight line until it accidentally strikes against some other molecule which may be moving in any

other direction. Hence it is obvious that the chance of the molecule ever coming back to its original position is indefinitely small. This applies especially to the case of the æther, the particles of which are comparable to those of the gravity-gas.

The above are a few very simple cases, in which it seems certainly difficult to avoid the conclusion that action at a distance must necessarily exist. And if it exists in these cases, then, as already remarked, it becomes at least probable that it may exist in other cases, such as gravity, where the evidence is not so clear. In conclusion it may be asked, therefore, what real reason is there why this hypothesis of action at a distance should not be admitted. To some minds it seems to present itself in the light of a theory which it is *à priori* difficult, if not impossible, to believe. But Physics has nothing to do with mental impressions; and in the history of the Inductive Sciences there are many well-known instances, where *à priori* notions of this kind have seriously hindered the advance of knowledge. It is evident that the progress of science in any direction must be towards certain universal and final facts, beyond which she cannot go. On the one theory, the ultimate fact in the case of gravity is enunciated in a very simple law of force, connecting together all ponderable bodies. On the other theory, the ultimate facts are apparently enunciated in the laws of impact between elastic bodies (which also involve the conception of force), and in the statement of the fundamental conceptions and results of the Kinetic Theory of Gases, assumed to hold for an exceedingly rare gas pervading all space. The writer submits that, *à priori*, one of these theories is as likely as the other—but that both must be judged by the test of their accordance with known facts, and by that test alone must be accepted or condemned.

On the general comparison of the two views, as to their power of explaining facts, one remark may perhaps be allowed. It will not, probably, be denied that, if we only knew the exact laws of any action whatever between bodies, we could at once explain it on the hypothesis that these bodies are made up of centres of force, each possessing position and inertia, and acting on the other centres according to laws which it would be

easy, or at least possible, to determine. It certainly cannot be said at present that we could equally explain any action by the mere laws of impact, even if we include in them those of elasticity. So long as these two statements hold, it seems more in accordance with the cautious spirit of true science to maintain the old theory, than unreservedly to adopt the new one.

XIV. *Note on* Prof. Exner's *Papers on Contact Electricity.* *By* W. E. Ayrton *and* John Perry*.

I. In the autumn of 1879 Prof. Fleeming Jenkin drew our attention to a paper by Prof. Exner, read before the Vienna Academy of Science, and appearing in the July number of their 'Transactions' for that year. This paper will also be found reprinted in this year's April number of Wiedemann's *Annalen der Physik und Chemie*; and quite recently an English translation, prepared by Mr. Brown, has appeared, in the October number of the Philosophical Magazine.

As then, this paper has been deemed of sufficient importance to be printed at least three times; and as the reasoning employed in it is of so plausible a nature as to mislead a casual reader, and to give him erroneous notions on the subject of contact electricity, we have thought it worth while to draw attention to the inaccuracies it contains.

The calculation given in the Phil. Mag. for 1851 by Sir Wm. Thomson of the electromotive force of a Daniell's cell, based on the principle of the conservation of energy, is of course well known. The method employed, which was due to Dr. Joule, is as follows:—The work done by a quantity of electricity Q passing between two points at a difference of potential E is EQ. Now if this electromotive force is produced by a Daniell's cell, the preceding quantity of work must be equal to the energy-equivalent of the chemical changes that take place in this cell when a quantity of electriciy Q passes through it. And since this latter can be determnied from the heats of combustion of the products decomposed and formed, and from a knowledge of Joule's mechanical equivalent of heat, Sir Wm. Thomson was enabled to

* Read November 13, 1880.

calculate the electromotive force of the Daniell's cell from the supposed known chemical reactions taking place in it. It has been pointed out by Dr. Wright*, and by others, that the great coincidence between the electromotive force of the Daniell's cell, thus calculated, and the value obtained by a direct measurement with an absolute electrometer would not have been arrived at by Sir William had he had at his disposal the more accurate determinations that have since been made of the heats of combustion. This, however, as we think may be gathered from Dr. Wright's paper, does not in the least disprove the accuracy or detract from the utility of Sir Wm. Thomson's, or rather Joule's, theory, but merely shows that the products of combustion in the Daniell's cell are not exactly what have usually been supposed; for it has to be remembered that if energy is developed or absorbed by occlusion of gases, or by any other physical action that has not hitherto been included in chemical actions, this must all be taken into account in the calculation of electromotive force.

II. Now Prof. Exner expresses the opinion that the so-called contact electricity is produced by the oxidation of the metals in contact with the oxygen of the air, in the same way as electricity is evolved by the oxidation of the zinc in galvanic cells. He says he has proved that this is true, and states, in consequence, that the electromotive force between two metals in contact with the air must be measured and expressed by the heats of combustion. The exact relationship which, in his opinion, ought to exist between the contact electromotive force of, say, zinc and copper and the difference of the heats of combustion of equivalent quantities of these metals is the fundamental part of his paper.

He says, at the bottom of page 598, Heft 4, Band ix. Wiedemann's *Annalen*, 1880, as we have translated it:—"We know that in cells each chemical process produces a potential-difference which is proportional to its heat-value; and in the case of the oxidation of a metal in air, we should expect that the potential-difference between a metal and the oxide produced would be proportional to the heat of combustion. Therefore any metal which, when insulated in the air, oxidizes,

* "On the Determination of Chemical Affinity in Terms of Electromotive Force," by C. R. Alder Wright, D.Sc., Phil. Mag. April 1880, p. 247.

must contain a certain quantity of separated positive and negative electricity; and it is obvious that these charges are inactive towards outside bodies. These separated electricities cannot surpass a certain tension-difference; for the observed tension is always a constant, no matter if the oxidation continues or not. From this it would appear that the quantities of electricity produced in excess through continual oxidation are neutralized again with the production of the corresponding quantity of heat.

"If now, for example, a piece of zinc through oxidizing in the air has a potential $+E$, the oxidized layer, or rather the layer of air which is in contact with it, has, on the contrary, the potential $-E$; so that the potential-difference is equal to $2E$, which must be measured by the heat of combustion of the zinc. If we now unite the zinc with any indifferent metal, for example platinum, then a part of the electricity will flow over to the platinum until both the metals have a common potential $+P$. The free tension on the zinc becomes now $-E+P$, that of the platinum $+P$; therefore the potential-difference between zinc and platinum is now $-E$, which is measured by half the heat of combustion of the zinc. If, therefore, the heat-value of the Daniell's cell be A (the heat-values, as is well known, must have reference to the chemical equivalents of the substances), and the heat of combustion of the zinc be B, then the potential-difference between zinc and platinum would be equal to $\frac{B}{2A}$. If the metal connected with the zinc is oxidized in the air, the manner of considering the subject still remains the same, or the potential-difference between the metals is measured by half the difference of the heats of combustion."

It will be observed that Prof. Exner speaks of the difference of potentials between a metal and its oxide as determinable from the heat of combustion; we presume, then, this difference must be a constant, what in fact he calls $2E$. Now let us consider the second part of his statement given above; and we find that by joining platinum metallically to zinc the platinum and zinc have a common potential which he calls $+P$; yet the difference of potential between the platinum and the oxide of zinc is now only $+E$, or half the previous

difference between zinc and its oxide. Although, then, he commences by saying that the difference of potential between zinc and its oxide is measured by the heat of combustion, which we know, per chemical equivalent, is a constant, he ends by concluding that the difference of potential is *not* a constant.

But it may be suggested that as his language is a little vague, and not in accordance with that employed in the modern mathematical theory of electricity, perhaps he means that there is a certain charge of electricity in the oxide which is a constant. This, however, does not appear to be his meaning, since a very simple consideration will show that if the charge of electricity in the oxide were a constant, the difference of potentials between zinc and platinum in metallic contact, as measured by the Volta experiments, would not be, as experiment shows, fairly constant for clean dry zinc and platinum (viz. 0·981 volt), but would be a variable depending on the condensing-arrangement employed.

[*Addition*, Dec. 21st.—This latter argument, Mr. Brown says, in the 'Electrician' for Dec. 4th, he does not follow. If, however, he will refer to Prof. Exner's own description of the measuring-apparatus employed, he will, by applying the ordinary mathematical laws, see that the method of attaching a Daniell's cell to the zinc and platinum plates in Volta's condenser, first with its poles one way and then reversed, measures, in terms of the Daniell's cell, the difference of potential between a point in the air close to the zinc plate and a point close to the platinum; but cannot possibly give any measurement of the actual electric charge in the zinc oxide or in Mr. Brown's "condensed compound gas-film," or in the platinum plate itself, unless we know the actual distance between the plates forming the condenser.]

III. We are justified, then, in concluding that he means that there is neither a constant difference of potentials between zinc and its oxide, nor a constant quantity of separated electricity. What, then, is his assumption? As far as an attentive study of his paper on our part can lead us, it is simply this:—The potential-difference between two metals in contact in air is measured by *half* the difference of the heats of combustion—an assumption which, in spite of the semblance of reasoning employed in the previous sentences, our

knowledge of electricity gives us no basis for making. But Prof. Exner's sets of experiments I., II., III., consisting of direct measurements with Kohlrausch's apparatus of the electromotive forces of contact of zinc and platinum, copper and platinum, and iron and platinum, combined with J. Thomsen's determinations of the heats of combustion, appear to lend a most powerful support to Prof. Exner's assumption. Are we not justified, then, in accepting it as a conclusion proved by experiment, although it could not have been previously arrived at from our existing knowledge of electricity? Now it is unfortunate for this conclusion that Prof. Hoorweg, in the *Annalen der Physik und Chemie*, No. 9, Band xi. Heft I. pp. 133–155, 1880, has taken exception to Prof. Exner's experiments themselves; and, to make this plain, he gives the following table:—

		Kohlrausch*.	Hankel.	Exner.	Ayrton and Perry (1880).
Zn	Pt . .	0·984	0·984	0·881	0·981
Cu	Pt . .	0·184	0·184	0·367	0·238
Fe	Pt . .	0·384	0·312	0·704	0·369

Our results as given above by Prof. Hoorweg are in terms of a volt, and not in terms of the electromotive force of a Daniell's cell, which is the standard employed by the previous observers. To reduce our numbers to the same standard, they must be diminished by about 10 per cent. They become then:—

		Ayrton and Perry.	
Zn	Pt . .	0·883	of a Daniell's cell.
Cu	Pt . .	0·214	
Fe	Pt . .	0·332	

From these numbers it will be seen that while Kohlrausch, Hankel, and ourselves, although making the experiments in quite different ways, and with necessarily different specimens of the metals, have obtained fairly consistent results, those of Prof. Exner, with the exception of the

* Prof. Exner says that since the time of Kohlrausch "only isolated and untrustworthy contact experiments have been made." As, however, those even carried out by Kohlrausch himself with metals appear to disagree with those of Prof. Exner, while they agree with the results obtained by other experimenters, Prof. Exner might consistently have included Kohlrausch's name in his sweeping condemnation.

first, stand by themselves. Nevertheless all his results agree with surprising accuracy with the numbers required by his theory.

IV. On page 597 of his paper, Prof. Exner refers to the early experiments of Pfaff, which proved that the measured electromotive force of contact of two metals was independent of the gaseous medium surrounding them, provided, of course, visible chemical action did not take place; and Prof. Exner states that the subsequent experiments of De la Rive, which he thinks proved that chemical action was necessary, negatived those of Pfaff. We have not been able to find any thing about Pfaff in the reference given by Prof. Exner, which is perhaps due to a misprint in the *Annalen*; but Pfaff's letter to Gay-Lussac, which we have come across in the *Annales de Chimie et de Physique*, vol. xli. pp. 236–247, 1829, gives an account of experiments made with as great accuracy as was possible with the instruments in use at the time, and which led to the result that the difference of potential, measured in Volta's way, between zinc and copper metallically connected was not influenced by atmospheres of dry or damp air, oxygen, nitrogen, carbonic-acid gas, hydrogen, and olefiant gas. This is still one of the most valuable papers in the history of contact electricity; and, with all due respect for Prof. Exner's opinion, we are compelled to attach much more faith to the careful work of Pfaff than to experiments of De la Rive, who, we find, actually coated his plates thickly with varnish to prevent oxidation, and, because with such plates he obtained but little difference of potentials, concluded that the well-known Volta effect was produced by oxidation. This experiment, indeed, is only equalled in vagueness by the one described by Prof. Exner at the end of his paper, made with silver in chlorine and silver in air, and which, as has been recently pointed out by Prof. Hoorweg, proved nothing but the well-known fact that silver chloride is an electrolyte. For Prof. Exner's arrangement was this:—"A short glass cylinder was closed air-tight at its upper end with a plate of silver, which did not, however, touch the glass, as there was a collar of paraffin-wax. The bottom of the vertical glass tube was closed air-tight with a cork, through which passed two small glass tubes to admit the gas and allow it to escape, and also a platinum wire

well insulated by paraffin-wax, and the inner end of which touched the silver plate. This latter was only for making metallic connexion with the condenser.

"A second silver plate, of the same dimensions as the first, could be placed on this condenser in the same way as in the earlier experiments.

"Now, if the condenser-plates were connected, there was naturally not the least charge. But as soon as the interior of the glass tube was filled with dry chlorine, the condenser showed at once a considerable and quite constant electromotive force."

Of course it did, we should reply, seeing that a galvanic cell had been formed of platinum, chloride of silver, and silver. If, however, the platinum wire had been soldered to the silver plate, instead of merely loosely touching it, no such effect would have been observed.

Prof. Exner refers to Mr. Brown's most interesting series of experiments*; but we feel that, although carefully made and faithfully described, they cannot throw much light on the relative values of the so-called contact and chemical theories. For Mr. Brown's zinc and copper plates were coated with zinc sulphide, copper sulphide, or zinc chloride and copper chloride; and every supporter of the contact theory is prepared to admit that there is a difference of potential between a metal and its oxide, chloride, or sulphide, or any other of its salts in a dry or wet state. In fact, in Sir Wm. Thomson's earliest experiments on contact, he refers to the great change produced in the measured difference of potentials of a point in the air close to the zinc, and of a point close to the copper, if the copper be allowed to oxidize†. Had Mr. Brown's apparatus enabled him to make quantitative experiments instead of only qualitative ones, his results would have been of great value in connexion with the electromotive forces of galvanic cells such as we have used, in which the ordinary water between the zinc and copper plates is replaced by glass, paraffin-wax, mica, shell-lac, &c.‡,

* "Theory of Voltaic Action," by J. Brown, Phil. Mag. Aug. 1878, pp. 142–145, and Feb. 1879, pp. 109–111.

† "New Proof of Contact Electricity," by Sir Wm. Thomson, Proc. Lit. and Phil. Soc. of Manchester, Jan. 21, 1862.

‡ "Contact Theory of Voltaic Action," Part II., by W. E. Ayrton and John Perry, Proc. Roy. Soc. No. 106, pp. 26–34, 1878.

or by dry metallic salts, such as have recently been employed by Prof. Hoorweg. Mr. Brown's experiments, however, must not be regarded as confuting Pfaff's work of 1829.

V. We are therefore reluctantly compelled to conclude that Prof. Exner's experiments described in his first paper are inaccurate, and that their striking agreement with his assumption is due to a fortuitous combination of errors. And it may be observed in passing, that the same kind of conclusion has been arrived at by Prof. Young, of Princeton, regarding the result communicated to the Vienna Academy of Sciences, that thermoelectricity is also due to oxidation, since he has recently shown* experimentally that the thermoelectric power of metals is the same in air at a millionth of an atmosphere as at ordinary pressures.

We may mention that, for the purpose of testing whether a gas has any important effect at all in contact action, we have for some time been arranging apparatus to try Volta's original experiments in a Crookes's vacuum.

VI. The succeeding paper of Prof. Exner's was given in the last December number of the Transactions of the Vienna Academy of Sciences, and again in No. 6, B. x. H. 2, pp. 265–284, of Wiedemann's *Annalen*. The ideas contained in it are, we think, based on some misconception of the contact theory of electricity. It has long been known that when the dilute acid of a simple cell is saturated with oxygen there is a primary great electromotive force, which diminishes as the evolved hydrogen begins to collect on the negative plate, not finding any more free oxygen to combine with. It has also been known that, if the metal from either plate is carried over and deposited on the other, the electromotive force of the cell goes down. Prof. Exner, however, sets himself to make careful experiments with a Smee's cell, in which deposition of zinc on the negative plate is rendered impossible by having the plates in separate vessels connected with a glass tube drawn out to a fine point; and he found that the primary electromotive force was 1·15 that of a Daniell's cell, and that it diminished after a current produced by short-circuiting had deposited hydrogen on the platinum plate—also that, whatever was the

* "On the Thermoelectric Power of Iron and Platinum *in vacuo*," by Prof. E. A. Young, Phil. Mag. vol. x. p. 450 (December 1880).

negative plate, there was the same working electromotive force. "The preceding results," says Prof. Exner, "connect themselves intimately with the consequences of the chemical theory; they contradict entirely the contact theory." For he reasons:—"The contact theory requires that the electromotive force of a Smee's element should begin with a value 0·73 of that of a Daniell's cell" [this is derived from the heat of combustion of zinc in oxygen, the combination of the oxide with sulphuric acid, minus the energy required for the decomposition of an equivalent quantity of water] "and then sink to a lower value, which depends on the amount of polarization—that is, on the amount of resistance,—and, further, that it depends on the nature of the negative plate. The chemical theory, on the contrary, requires that the Smee's element should first have an electromotive force between 0·732 and 2·15 of that of a Daniell" [2·15 is derived from only considering the heat of combustion of zinc with oxygen and the combination of the oxide with sulphuric acid], "and that this value should fall to 0·732 of a Daniell and then remain perfectly constant, no matter what be the metal forming the negative plate, as long as it does not give rise to chemical changes. Further, the value 0·732 of a Daniell must also depend on the resistance of the element."

Now what is correct in this was all given by Sir Wm. Thomson as far back as 1851; but the greater part is incorrect.

First, it is quite a mistake to say that "the contact theory requires that the electromotive force of a Smee's element should begin with a value 0·73 of that of a Daniell's cell." What the "*summation law*"* of the contact theory says is, that the electromotive force of a complete cell is equal to the algebraical sum of all the differences of potential, each measured separately, at the separate contacts—of metals with any layer of gas on them, gas with liquid, one liquid with another, &c.; and what these latter are in a Smee's water element, for example, can be found from the table at the end of our paper†.

* "Contact Theory of Voltaic Action," Part I., by Professors W. E. Ayrton and John Perry, Proc. Roy. Soc. No. 186, p. 23, 1878.

† "Contact Theory of Voltaic Action," Part III., by Professors W. E. Ayrton and John Perry, Phil. Trans. Roy. Soc. part i. pp. 15–34, 1880.

For, taking water, we have

Pt	$\mid H_2O$ . .	0·285 to 0·345 volt*,	
H_2O	$\mid$ Zn . .	−0·156 „ 0·105	„
Zn	$\mid$ Pt . .	0·981 „ 0·981	„
		1·110 to 1·431 volt,	
	Mean . . .	1·270 volt,	

or about what Exner found it for a dilute sulphuric-acid Smee's cell†.

Secondly, as regards the variations of the electromotive force of a Smee's cell, Sir Wm. Thomson calculated‡ from Dr. Andrews's experiments that, if we consider the oxidation of the zinc and the combination of this oxide with strong sulphuric acid, minus the energy necessary to decompose the equivalent quantity of water, we obtain as the electromotive force of a Smee's cell 2,056,200 British absolute units, which corresponds with 0·82 Daniell [with more modern data Exner gives 0·73], since the electromotive force of a Daniell's cell as determined experimentally by Joule is 2,507,100 British absolute units. Sir William adds:—"It is to be remarked that the external electromotive force determined for a single cell of Smee accord-

* The variations observed in measuring the electromotive force of contact of a metal and a liquid are due to the effect of gas absorbed, and being absorbed, by the liquid &c., and will always be noticed if the measuring-apparatus be only sufficiently delicate. Such differences have nothing in common with the great discrepancies referred to at the commencement of this note, on the results obtained by Prof. Exner and by other experimenters for the electromotive force at the contact of metals, since the latter is fairly constant at a constant temperature, so that any great discrepancies in such measurements can only arise from errors in experimenting.

† We are unable, from our results at present published, to calculate exactly the electromotive force of Smee's dilute-acid cell, since, as regards liquids, it was only with distilled water and with strong acids that the electromotive force of contact of platinum was measured in our experiments. We can, however, from these latter approximate to limiting values of the electromotive force of a Smee's dilute-acid cell; that is, using the values of the contact electromotive forces of platinum with water and with strong sulphuric acid, and assuming that the contact of platinum with dilute sulphuric acid is somewhere between these two, it follows that the electromotive force of a Smee's dilute-acid cell, as determined from the sum of the separate contact differences of potential, must at first be greater than 1·567 volt.

‡ "On the Application of Mechanical Effect to the Measurement of Electromotive Forces," by Prof. Thomson, Phil. Mag. Dec. 1851.

ing to the preceding principles, by subtracting the chemical resistance" [this latter being due to the evolution of hydrogen upon the platinized silver] "from the value $J\theta\epsilon$, is the *permanent working* external electromotive force. The electrostatical tension which will determine the initial working external electromotive force depends on the primitive state of the platinized silver plate. It could never be greater than to make the initial working force $J \times 1670 \times \epsilon$, or 5,444,500" [2·17 Daniells according to the above reduction], "corresponding to the combination of zinc with gaseous oxygen, and of the oxide with sulphuric acid. It might possibly reach this limit if the platinized surface had been carefully cleaned and kept in oxygen gas until the moment of immersion, or if it had been used at the positive electrode of an apparatus for decomposing water immediately before being connected with the zinc plate; and then it could only reach it if the whole chemical action were electrically efficient, and if there were no chemical resistance due to the affinity of the platinized surface for oxygen.

"It is also to be remarked, that the permanent working electromotive force of a galvanic element consisting of zinc and a less oxidizable metal immersed in sulphuric acid can never exceed the number 2,056,200, derived from the *full* thermal equivalent for a single cell of Smee's, since the chemical action is identical in all such cases, and the mechanical value of the external effects can never exceed that of the chemical action. In a pair consisting of zinc and tin, the electromotive force has been found by Poggendorff to be only about half that of a pair consisting of zinc and copper, and consequently less than half that of a single cell of Smee's."

The alteration in the electromotive force of galvanic cells produced by gas dissolved in the liquid has been known for a long time, indeed before the experiments of De Fonville, De Lerain, Marié-Davy, referred to by Prof. Exner; and we may draw attention to some experiments of our own, which show that the polarization phenomena in voltameters are wonderfully influenced by the state of the platinum plates and the liquid as regards absorbed gas*.

* "A Preliminary Account of Reduction of Observations on Strained Material," &c., by John Perry and W. E. Ayrton, Proc. Roy. Soc. No. 30, pp. 411–435 (1880).

Thirdly, Prof. Exner states that the contact theory requires that the permanent electromotive force of a Smee's should depend on the nature of the negative plate, while the chemical theory requires that it should be independent of the negative metal; further, that his experiments agree with the latter conclusion and disagree with the former. Now the first part of this statement is wrong; for the contact theory does not require *per se* that the electromotive force should, or should not, depend on the negative metal. What the contact theory tells us is that the electromotive force of the cell will depend on the electromotive force of contact of every pair of dissimilar substances in the circuit, and therefore will depend, among other things, on the contact difference of potentials of the negative metal with possibly a gas, the gas with the liquid, the liquid possibly with another gas, the gas with the positive metal, and the positive metal with the negative. Further, the conclusion itself to which Prof. Exner has arrived, viz. that the working electromotive force of a Smee's cell does not depend on the negative plate, has, like his other conclusions, been disputed. For Beetz * has recently published the results of experiments with simple cells; and his electromotive forces are:—

Zinc and platinum.		Zinc and copper.		Zinc and silver.	
Open.	Closed.	Open.	Closed.	Open.	Closed.
1·52	0·72	0·98	0·46	1·23	0·57

And when he used sodium amalgam the difference of the electromotive forces of the closed cells was equally striking :—

Sodium amalgam and platinum.		Sodium amalgam and silver.		Sodium amalgam and copper.		Sodium amalgam and zinc.	
Open.	Closed.	Open.	Closed.	Open.	Closed.	Open.	Closed.
2·31	1·33	2·05	1·22	1·79	1·14	0·78	0·68

The nature of the negative metal must always have a great effect on the initial electromotive force; we are, however,

* "On the Nature of Galvanic Polarization," by W. Beetz, *Annalen der Physik und Chemie*, B. x. H. 3, pp. 348–371 (1880).

astonished that Prof. Beetz should find such great differences in the columns headed "closed." Our impression has always been that when the negative metal becomes sufficiently coated with hydrogen, the contact between the thin conducting-layer of gas and the metal was almost like that of a pair of metals; and if this is the case, then

$$H \mid Pt + Pt \mid Zn$$

is the same as

$$H \mid Cu + Cu \mid Zn,$$

and almost any negative metal would eventually act like a conducting hydrogen plate.

Prof. Exner's second paper, like his first, we are compelled to regard as wrong theoretically, and describing experiments which do not lead to the conclusions he has deduced from them.

It is not necessary for us to follow Beetz into his disproof of Prof. Exner's statements regarding the use of the word polarization, which is employed in England in the vaguest way to indicate a change of current whether from alteration in the electromotive force or in the resistance, but to which in Germany various philosophers attach distinct meanings. Between the contact theory as properly understood and the chemical theory there is really nothing antagonistic. The "summation law" deduced from various experiments for metals and one liquid, and extended by our own experiments to two or more liquids, tells us that the electromotive force of any arrangement is equal to the algebraical sum of all the separate differences of potential at the various surfaces of contact of dissimilar substances, each difference of potential being measured by an induction method such as we have described and used. The chemical theory tells us that the energy given out in any electric circuit must be equal to the consumption of chemical energy in the circuit. The electromotive force, then, in any circuit can either be calculated on the contact theory, if we know *each of all* the differences of potential at the various surfaces of separation of dissimilar substances (solid, liquid, or gaseous) in the circuit, or it may be calculated on the chemical theory, if we know exactly what are *all* the physical and chemical changes taking place and the heat-equivalent of every one of them. And the amount of the

electromotive force determined in either of these two ways must be identical.

The question of the relative delicacy of the two methods is a totally different question. Any balance accurately made will weigh accurately; but one form of chemical balance is more delicate than another: so, in the same way, there is every reason for believing that an electric test is a far more delicate test of chemical action than the analytical methods employed by the chemist. For example, the action of even small quantities of paraffin-wax on metal, which would quite escape the test of a chemical analysis, we have not only detected, but even measured, with an electrometer*.

XV. *Specific Refraction and Dispersion of Isomeric Bodies.* By J. H. GLADSTONE, *Ph.D.*, *F.R.S.*†

AMONG the properties of a body which are least liable to change, and which are the most capable of throwing light on its molecular constitution, is its specific refraction. This is the refractive index minus unity divided by the density or $\frac{\mu-1}{d}$.

In early papers on the subject‡, this specific refraction (or "specific refractive energy," as it was then called) was shown to be a constant, unaffected, or nearly so, by change of temperature, by the passage from the liquid to the solid or even gaseous condition, by mixture with other liquids, or by solution, or even (within certain limits) by changes of chemical combination.

In regard to changes of temperature, however, it was observed at the very commencement that there was "some influence, arising wholly or partially from dispersion,"§ which interferes with the exactitude of the law. In order to obviate this, if possible, the calculations were made for the least-refrangible limit of the spectrum, according to the

* "Contact Theory of Voltaic Action," Part II., by Profs. W. E. Ayrton and John Perry, Proc. Roy. Soc. No. 186, pp. 26–34, 1878.

† Read on November 27, 1880.

‡ Phil. Trans. 1863, p. 323, and 1869, p. 9; Journ. Chem. Soc. 1865, p. 108; Landolt, Pogg. *Ann.* cxxii. p. 545; Wüllner, *ibid.* cxxxiii. p. 1.

§ Phil. Trans. 1863, p. 323.

formula of Cauchy. But it was found that these gave results little, if at all, more exact than those for the line A of the solar spectrum. In our subsequent work, Mr. Dale and I did not consider it worth while to go through the labour of this calculation; and my observations are always reckoned, if possible, for the line A, whilst Landolt has preferred the α of hydrogen gas, which is identical with the solar line C.

In regard to the passage from one state of aggregation to another, the few cases that have been directly observed are fairly in accordance with the law*.

In the case of mixtures of liquids†, the conclusion that the specific refraction of a mixture of liquids is the mean of the specific refractions of its constituents is a near approximation, if not an absolute truth.

With regard to the influence of solution, some doubt has recently been thrown upon the deductions drawn from dissolved salts or other chemical compounds; but the general, if not absolute, correctness of the method is supported by a very large amount both of direct proof and collateral evidence ‡. As an instance of the latter, I may quote the last observations made in my laboratory. The specific refraction of pyrene, $C_{16}H_{10}$, as determined from its solution in benzol, in chloroform, and in carbon disulphide, is respectively

·6235, ·6252, ·6240,

a practical agreement which could scarcely happen if the method were erroneous. Taking the mean of these numbers, and multiplying it by the atomic weight, we obtain, as the refraction-equivalent of pyrene, the very high figure of 126·1.

In regard to chemical combination, it is now well understood that an elementary substance such as carbon will exert the same retarding influence upon the rays of light throughout a very large number of its compounds, whilst in others it may exert a different influence. This has naturally attracted the attention of organic chemists to the subject, and promises to be a very fruitful field of investigation.

In the present communication I intend to confine my remarks to those groups of bodies which exhibit isomerism. It is well

* Phil. Trans. 1869, pp. 10, 11.

† Phil. Trans. 1863, p. 332; Landolt, *Ann. Chem. Pharm.* iv. (Sup. Bd.) 1865, p. 1.

‡ Phil. Trans. 1869, pp. 14, 15.

known that two or more compound bodies, differing from one another in physical or chemical properties, may be composed of the same elements in precisely the same proportions. In such a case the specific refraction may be the same, or it may be different.

It is found to be the same notwithstanding differences of other optical properties, differences of molecular weight, and differences of chemical properties.

1st. *Differences of other optical properties.*—It so happens that among the bodies which display the phenomena of circular polarization, there are several isomeric groups, and that different members of these groups differ from one another in their effect on the polarized ray. Thus with respect to the different terpenes, $C_{10}H_{16}$, some of them rotate the plane of polarization to the right and others to the left, and that to different degrees; yet they have all practically the same specific refraction, 0·537*.

It was also an early observation that solutions of cane-, grape-, and honey-sugar, and gum, of the same strength, though they differ largely in their effect on polarized light, give the same, or very nearly the same, refraction and dispersion†.

Again, it is well known that tartaric acid is an optically active substance, and racemic acid optically inactive, while their chemical composition, $C_4H_6O_6$, is identical. The following table gives the specific refraction and dispersion of these two acids in solution as deduced from data previously published‡. The specific dispersion is the difference between the specific refraction for the line A and that for the line H, or, which is the same thing, $\frac{\mu_H - \mu_A}{d}$.

	Specific refraction.	Specific dispersion.
Tartaric acid.....	·3020	·0131
Racemic acid.....	·3036	·0143

Carvol and menthol, the odorous principles of caraway and mint respectively, are very definite substances, of the compo-

* Chem. Soc. Journ. 1864, p. 18. † Phil. Trans. 1863, p. 332.
‡ Ibid. 1869, p. 30.

sition $C_{10}H_{14}O$; but the first rotates the plane of polarization very powerfully to the right, and menthol very powerfully to the left; yet they have practically the same specific refraction *.

	Specific gravity.	Specific refraction.	Specific dispersion.
Carvol from caraway	0·9530	·5126	·0362
„ from dill	0·9562	·5115	·0348
Menthol.....	0·9394	·5100	·0331

2nd. *Differences of molecular weight.*—Interesting cases of this are to be found among the essential oils, as shown in the subjoined table, in which the numbers given for the *terpenes* are the mean of ten different specimens, for the *citrenes* of twelve specimens, and for the *cedrenes* of eight specimens, each group probably consisting of several isomerides †.

	Specific gravity.	Specific refraction.	Specific dispersion.	Refraction-equivalent.
Terpenes, $C_{10}H_{16}$	0·8600	·5370	·0302	73·03
Citrenes, $C_{10}H_{16}$	0·8466	·5475	·0336	74·46
Cedrenes, $C_{15}H_{24}$	0·9166	·5392	·0307	110·00
Colophene, $C_{20}H_{32}$	0·9391	·5413	·0329	147·23

The terpenes and citrenes show a constant though not a large difference in specific refraction; but the polymeric bodies of the same series seem to have so nearly the same specific refraction as the terpenes that the differences may be attributed to impurities or experimental error. The refraction-equivalents of the three groups are of course very nearly in the proportions of 2, 3, and 4.

3rd. *Differences of chemical properties.*—In the cases already mentioned it is possible that the differences of physical properties depend upon some difference in the arrangement of the ultimate atoms; but there are other cases in which this is perfectly well known to be the case. Isomeric bodies of this nature are more strictly termed metameric. Delffs showed, as far back as 1850‡, that such pairs as formic ether and acetate of methyl, both of the ultimate composition $C_3H_6O_2$, had the same refraction; whilst the papers of Landolt, and the more recent ones of Brühl §, abound in instances. Among the

* Chem. Soc. Journ. 1872, p. 9.
† Chem. Soc. Journ. 1864, p. 18.
‡ Pogg. *Ann.* lxxxi. p. 470.
§ Liebig's *Ann.* cciii. pp. 1, 255.

observations in my notebook, hitherto unpublished, occur the following :—

	Specific refraction.	Specific dispersion.
Propyl iodide. C_3H_7I	·2844*	·0216
Isopropyl iodide, „	·2883*	
Cresol from thymol, C_7H_8O.....	·5116	·0454
Metacresol, „	·5091	·0452
Benzylic alcohol, „	·5069	·0415
Nitrobenzoic acid (α), $C_7H_5(NO_2)O_2$.....	·3994	
„ „ (β), „	·4004	
Benzylic butyrate, $C_{11}H_{14}O_{12}$	·4777	·0332
„ isobutyrate, „	·4805	·0331
Monochloro-toluol, C_7H_7Cl	·4807	·0409
Benzyl chloride, „	·4836	·0409

Though identity of ultimate composition will generally produce identity of specific refraction, there are certain cases in which isomeric (or, rather, metameric) bodies differ widely in their power of retarding the transmitted ray. The earliest of those observed was the case of aniline and picoline, C_6H_7N; and as Dr. Thorpe has kindly lent me his specimen of picoline, I am able to confirm the previous determinations.

	Specific refraction.	Specific dispersion.
Aniline	·550	·0635
Picoline (*C. G. Williams*) ...	·513	·0448
„ (*Thorpe*).....	·522	·0431

The difference in this pair was originally attributed to the fact that the two bodies "are constructed very differently;" and in subsequent papers it was pointed out that, when the atoms of carbon were not saturated in the usual way, there is an augmentation in their refractive power, analogous to what happens when an element such as iron changes its valency†. Brühl has expressed this more definitely by putting forward the theory that, whenever two carbon atoms are doubly linked, there is an increase of the refraction-equivalent amounting to

* Brühl gives the values 0·2873 and 0·2907 respectively for the line C.

† Phil. Trans. 1863, p. 333; Chem. Soc. Journ. 1870, p. 150; Proc. Royal Instit. March 1877.

2·0 for the limit of the spectrum, as reckoned by Cauchy's formula, or about 2·2 for the hydrogen-line α, and of course a little less than 2·2 for the line A. I have no doubt that both Brühl himself and other chemists will have much to say in the future as to the extent to which this theory may be in accordance with present views of the constitution of the various organic compounds.

In my notebook I find the following instances of isomeric bodies which differ in specific refraction :—

		Specific refraction.	Specific dispersion.	Refraction-equivalents.
Acetone,	C_3H_6O.....	·4420	·0207	25·64
Butyric ether,	$C_6H_{12}O_2$	·4402	·0191	51·06
Allyl alcohol,	C_3H_6O.....	·4734	·0275	27·45
Carvol,	$C_{10}H_{14}O$	·5122	·0355	76·83
Thymol,	„	·5206	.....	78·09
Nitraniline (α),	$C_6H_6(NO_2)N$	·469	.....	64·72
„ (β),	„	·546	.....	75·34
Cresylic acetate,	$C_9H_{10}O_2$	·4677	·0348	70·15
Benzylic acetate,	„	·4945	·0394	74·17
Phenyl-ethyl acetate,	$C_{10}H_{12}O_2$.....	·4776	.....	78·32
Hydrocinnamene acetate,	„	·5183	·0382	85·00

Acetone and allylic alcohol have been compared already by Brühl, with similar results, and form one of the striking cases on which his theory depends. The refraction-equivalent of thymol being 6·8 above the normal, is confirmatory of the position which is now given to it in the great aromatic group—a position which I was disposed to assign to it ten years ago, on the evidence of its optical properties.

The two nitranilines were lent to me by Dr. Mills. Unfortunately they are very sparingly soluble bodies; and the above figures, though each of them the mean of three observations, are only given as approximately correct. But that they are really different there can be no doubt.

The two pairs of acetates were lent by Dr. Hodgkinson; and the last one is of particular interest, on account of the cinnamene compound having a higher refraction-equivalent than can be accounted for by any existing theory.

Specific Dispersion.

Though there are several sources of error in determining indices of refraction for the line A or for the line H, the actual distance between these two may be measured with great exactness, and the experimental error rarely, I believe, exceeds 0·0002. The possible error in the determination of the density at the same temperature has also to be considered with regard to specific dispersion; but any inaccuracy in the figures above given will certainly be confined to the fourth place of decimals.

Among the conclusions that may be drawn in regard to dispersion are the two following :—

1st. Where the carbon atoms are exerting a more than normal influence on the refraction of the rays of light, there is a great increase of dispersion. It was pointed out some years ago that the aromatic bodies have a great dispersive power *, and that "dispersion, as well as refraction, increases very rapidly with the number of atoms of carbon that are not combined with at least two of hydrogen or their equivalent."† Evidence of this is to be found both in the older and the more recent researches, whether in this country or on the Continent, and is always accumulating. Confining our attention to the figures given in this paper, it will be observed that in cases where the carbon is normal the specific dispersion is expressed by low figures (the highest of which is, in fact, acetone, ·0207); while in the isomeric allylic alcohol, which has a higher refraction, it rises at once to ·0275. The essential oils and their congeners, and such bodies as cresylic acetate, are above ·0300; while the purely aromatic compounds are all above ·0400.

2nd. Where isomeric bodies have the same or nearly the same specific refraction for the line A, they have the same also for the line H. The apparent deviations from this rule I am disposed to attribute to experimental error, and still more to impurity of substance. It is clear that in many cases of carbon compounds the presence of a differently constituted body would reveal itself by its influence upon dispersion more than upon refraction.

* Journ. Chem. Soc. 1870. † Proc. Roy. Inst. March 1877.

XVI. *On the Determination of Chemical Affinity in terms of Electromotive Force.*—Part III.* *By* C. R. Alder Wright, *D.Sc.* (*Lond.*), *Lecturer on Chemistry and Physics in St. Mary's Hospital Medical School.*

On the Absolute Values of the Ohm and of the Mechanical Equivalent of Heat, and on the Nature of Polarization and Electrolysis, and the amount of work done when the latter occurs.

55. Since the publication of Parts I. and II. of these researches, it has been obligingly pointed out by Mr. L. B. Fletcher, of Baltimore (Phil. Mag. [5] x. p. 436), that, by a slip, it is stated in § 35 that the values of the B.A. unit of resistance deducible from the 1867 experiments of Joule and from those detailed in Part II., are from 1·5 to 2·0 per cent. *above* one earth-quadrant per second, instead of that amount *below* this theoretical value, it being assumed that the mean water-friction value of Joule (41·555 megalergs, § 34) is correct; and Mr. Fletcher also states that the first results of an experimental redetermination of the absolute value of the ohm, on which he is now engaged, are similar in character. Besides the valuations of Lorenz and Kohlrausch, briefly referred to in Part I. as illustrations of the want of absolute certainty as to the true value of the B.A. unit, two other sets of observations on this point have been made within the last two or three years—one by Prof. H. A. Rowland (Silliman's Journal [3] xv. pp. 281, 325, and 430, 1878), and the other by H. F. Weber (Phil. Mag. [5] v. pp. 30, 127, and 189, 1878). By making observations of the value of the current induced in one coil by the establishment of a measured current in another one, Rowland obtained values of the resistance of the former such that, by comparison with four copies of the B.A. unit (or a multiple thereof), the following numbers were obtained as the resistance of the latter:—

		Earth-quadrant per second.
Coil No. 1.	B.A. unit, by Elliot . . .	0·99257
„ 2.	10-ohm coil, „ . . .	0·98963
„ 3.	10-ohm coil, by Warden, Murhead, and Clark . . .	0·99129
„ 4.	100 „ „ „	0·99098
	Mean	0·99112

* For Part I., see vol. iii. p. 213; Part II., vol. iii. p. 246.

Hence, on the whole, Rowland's experiment indicates an error in the B.A. unit of 0·00888=0·888 per cent. *in deficiency.*

Weber's determinations, on the other hand, indicate that the B.A. unit is nearly correct, the slight error being one of excess, and that the value of J is somewhat above that deduced from Joule's water-friction experiments. Thus he obtained the following values for J in gravitation measure; the annexed values in ergs are calculated on the supposition that at Zurich the value of g is 981·5.

	Gravitation measure.	Megalergs.
Value derived from calculations based on the different specific heats of a gas, from experimental determinations by Regnault and Röntgen	428·95	42·10
Value derived from experiments by H. F. Weber, on the heat developed by a known current whilst passing through a resistance measured in absolute measure by himself	428·15	42·02

Taking the mean of these values for J (=428·55 in gravitation measure), and determining the heat produced by a measured current in a circuit the resistance of which was measured by himself in absolute units, Weber obtained a mean value for the Siemens unit of resistance of $0{\cdot}9550\times10^9$ C.G.S. units, employing a coil (No. 1914) obtained from W. Siemens as standard. By two other different methods (one depending on the determination of the rate of oscillation of a magnetic needle in a coil, the other on the measurement of the current induced in a given coil by opening a known current in an adjacent circuit) the resistance of this same standard coil was found to be respectively $0{\cdot}9545\times10^9$ and $0{\cdot}9554\times10^9$, giving as final average of the three series of observations, $0{\cdot}9550\times10^9$ C.G.S. units. Unfortunately Weber did not compare his standard Siemens unit with any copy of the B.A. unit: assuming, however, that the Siemens unit used by him bore to the B.A. unit the same ratio as that found by Kohlrausch (§ 36), viz. 1 to 1·0493, the value of the B.A. unit becomes

finally

$$0{\cdot}9550 \times 1{\cdot}0493 = 1{\cdot}0021 \text{ earth-quadrant per second,}$$

exhibiting an error in excess of $0{\cdot}0021 = 0{\cdot}21$ per cent.

Taking these results into consideration along with those of Kohlrausch and Lorenz, discussed in Part II., the following values are finally deducible for the Siemens and B.A. resistance units respectively in earth-quadrants per second:—

	Siemens unit.	B.A. unit.
B.A. Committee	0·9530 (*a*)	1·0000
Kohlrausch	0·9717	1·0196
Lorenz	0·9337	0·9797 (*b*)
Rowland	0·9446 (*a*)	0·99112
H. F. Weber, 1st method . .	0·9550	1·0021 (*b*)
2nd „ . . .	0·9545	1·0016 (*b*)
3rd „ . . .	0·9554	1·0025 (*b*)

the values marked (*a*) for the Siemens unit being derived from the observed value of the B.A. unit by dividing by 1·0493, the ratio found by Kohlrausch, and those marked (*b*) for the B.A. unit being obtained by multiplying the observed values of the Siemens unit by 1·0493. Mr. Fletcher's preliminary results as above stated give a value less than 1·0000. Taking all these valuations into consideration, it would seem that, in the existing state of our knowledge, it is just about as probable that the B.A. unit is in error in deficiency as that it is erroneous in excess. Accordingly, in the following experiments it is assumed that the B.A. unit represents exactly one earth-quadrant per second, and in consequence that the E.M.F. of a Clark's cell is exactly, as determined by him, $1{\cdot}457 \times 10^8$ C.G.S. units, or 1·457 theoretical volt.

56. Admitting this to be so, however, it does not seem to be possible that Joule's water-friction values of J are exact (§ 34): not only do the determinations of Hirn and Violle concur in indicating values for J of from nearly 2 to 3 per cent. higher than these water-friction values (§ 37), but, further, four different sets of observations also indicate that if the B.A. resistance-unit be correct (*i. e.* if it = 1 earth-quadrant per second), or if the Siemens unit be 0·9530 earth-

quadrant per second, the value of J must be from 1 to 2 per cent. higher than these values, and, on the whole, upwards of 42 megalergs. These observations are, first, those of von Quintus Icilius (Pogg. *Ann.* ci. p. 65) as corrected by H. F. Weber (*loc. cit. suprà*), which were based on an erroneous early determination of the absolute value of a Jacobi resistance-unit by W. Weber; after correction they indicate a value for J of 431·6 in gravitation measure, or, assuming $g=981$, of 42·34 megalergs; and, next, those of Joule himself, those of H. F. Weber above quoted, and those of the author and Mr. Rennie (Part II.), which yield the following results:—

	Value of J, the B.A. unit being supposed to be exactly 1 earth-quadrant per second.
Von Quintus Icilius (corrected by H. F. Weber)	about 42·34 megalergs.
Joule (1867, *vide* § 33), the results of which investigation have been shown to be too low (§ 54) .	above 42·10 „
H. F. Weber*, $42{\cdot}02 \times \frac{1{\cdot}0000}{1{\cdot}0021}$ . .	41·93 „
Alder Wright and Rennie (value slightly too low)	above 41·96 „

Moreover, as stated above, H. F. Weber has calculated, from Regnault's and Röntgen's experiments on the specific heats of air &c., that J=42·10 megalergs. Hence, finally, taking into account all the above experiments, the most probable value of J lies close to 42 megalergs, being above rather than below that value. Until further authoritative determinations finally settle the question as to the true values of the B.A. unit and of J, the former may, as above stated, be considered to be exactly 1 earth-quadrant per second, and the latter may be safely taken as being 42 megalergs, most probably lying between 41·75 and 42·25 megalergs. In the following parts of this paper, consequently, J is taken $= 42 \times 10^6$ C.G.S. units,

* Weber's result refers to air-thermometer temperatures, those of the other experimenters to temperatures measured by the mercurial thermometer and not reduced to air-thermometer readings.

$\alpha\chi J$, the factor for reducing gramme-degrees to E.M.F. units (volts), is taken as being $=0{\cdot}000105\times 42\times 10^6=4410{\cdot}0$.

General Conclusions from the results of previous experimenters, and those subsequently detailed: Statement of Theorem relative to Polarization and the Nature of Electrolysis and the Amount of Work done therein.

57. It has been shown in Part I. (§§ 13–17) that the work expended in decomposing an electrolyte into the "nascent" products of electrolysis is not necessarily the same as that performed in breaking it up into the final products of electrolysis, and that by determining (in terms of E.M.F. or otherwise) the two quantities, conclusions may be drawn as to the general nature of the phenomena connected with the "nascent state." If the difference of potential between the electrodes of an electrolytic cell be E, during the passage of a quantity of electricity Q sufficient to decompose a gramme of electrolyte in a time t (thereby giving rise to a current $C=\frac{Q}{t}$) a total amount of work $EQ=ECt$ is done, of which $C^2Rt=CQR$ represents the work done as heat due to the resistance of the cell R (Joule's law, Part I. §§ 1 & 2); consequently an amount $EQ-C^2Rt=(E-CR)Q$ of work is done in decomposing the electrolyte into the nascent products of decomposition. The E.M.F. $E-CR$ representing this amount of work is readily measurable by electrical means; for it is the quantity sometimes spoken of as the "counter E.M.F. set up during electrolysis," being the value of e in Ohm's theorem

$$C=\frac{\Sigma(E)-e}{\Sigma(R)+R},$$

where $\Sigma(E)$ is the sum of the electromotive forces of the battery, e the counter E.M.F. set up, $\Sigma(R)$ the total resistance in circuit less that of the electrolytic cell, and C the current produced. For if r be the "resistance of a wire obstructing the current equally with the electrolytic cell" (*i. e.* what may be conveniently termed the *apparent* resistance of the voltameter, equal to that of a wire through which the current C would pass when a difference of potential E subsisted between its ends), we have

$$C=\frac{E}{r}=\frac{\Sigma(E)-e}{\Sigma(R)+R}=\frac{\Sigma(E)}{\Sigma(R)+r};$$

whence*

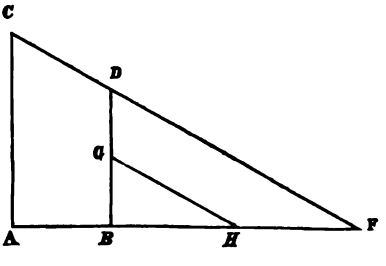
$$\text{C also} = \frac{E}{r-R} = \frac{\Sigma(E)-E}{\Sigma(R)} = \frac{E-e}{R},$$

and

$$e = E - CR.$$

58. Very many experiments have been made during the last thirty or forty years on the values of e under varying conditions, on a somewhat closely allied thing, viz. the E.M.F. existent between the electrodes of an electrolytic cell *after rupture of the current*†, and on the E.M.F. of gas-batteries (and especially those with hydrogen and oxygen as gases)‡.

* These relationships may be represented graphically thus:—On a base-line A B H F let fall perpendiculars A C, B D, representing respectively $\Sigma(E)$ and E, the length A B representing $\Sigma(R)$. Join C D, and produce the line C D till it cuts A B produced in F. Cut off from B D at the end D a length D G representing e, and through G draw G H parallel to C D F, cutting A F in H. Then B F represents r, and B H represents R. And by similar triangles,



$$\frac{AC}{AF} = \frac{AC-BD}{AB} = \frac{AC-DG}{AH} = \frac{BD}{BF} = \frac{BG}{BH} = \frac{DG}{HF},$$

or

$$\frac{\Sigma(E)}{\Sigma(R)+r} = \frac{\Sigma(E)-E}{\Sigma(R)} = \frac{\Sigma(E)-e}{\Sigma(R)+R} = \frac{E}{r} = \frac{E-e}{R} = \frac{e}{r-R}.$$

† The term "polarization" is sometimes applied to mean the counter E.M.F. of an electrolytic cell e as above defined, sometimes the E.M.F. set up between the electrodes after the current has ceased to flow (a quantity always less than the value of e existent whilst the current passes), and sometimes (perhaps most frequently of all in a vague undefined sense), to express the fact that something or other takes place tending to diminish the current: thus the silver plate of a Smee's cell is said to become "polarized." In the subsequent parts of this paper the terms "counter E.M.F. of an electrolytic cell" and "subsequent polarization" respectively are used to indicate the first two of these meanings.

‡ At the request of the Publication Committee of the Physical Society a discussion of the results obtained by many previous observers bearing in these directions is omitted, together with the numerous references to their

From these researches it results that, other things being equal, the counter E.M.F. set up during electrolysis increases with the current-strength as the size of the electrodes is diminished and as the temperature is lowered, at least within certain limits. The observations made have almost invariably been performed with currents of moderate or considerable magnitude; with such currents in no case has a value for e been obtained less than the E.M.F. corresponding to the decomposition into the final products, whilst with powerful currents much larger values have been obtained: thus with water, all values of e registered lie above 1·50 volt, and sometimes exceed 3 volts (when reduced to that unit). Certain experiments of Andrews (Phil. Mag. [3] x. p. 433), and Buff (*Ann. Chem. Pharm.* xciv. p. 1), made by decomposing water with a feeble battery-power (less than 1·50 volt), appear, however, to show that a less value for e may exist when a very minute current only is employed, in which case simultaneous evolution of hydrogen and oxygen does not take place; if the one or the other be prevented from making its appearance as a free gas by using a large electrode and a minute one (Wollaston's point), a feeble evolution of gas may be noticed (especially at first) from the small electrode, but none from the other. Similarly, the experiments of Helmholtz on what he terms "electrolytic convection" (Phil. Mag. [4] xlvii. p. 152), and analogous observations of others, show that, if the one or the other gas is suppressed by the chemical action of other kinds of gas respectively dissolved in the fluid surrounding the electrode or adherent to the electrode surface, water may be decomposed by an E.M.F. of less than 1·50 volt.

59. As regards "subsequent polarization," or the E.M.F. existent between the electrodes of an electrolytic cell after the original current has been ruptured, even when measured by a quick-working switch or "wippe," it results from the observations at present on record that a more or less perceptibly smaller value is always obtained than corresponds to the counter E.M.F. set up whilst the current was passing.

work. The best *résumé* of this work that the writer is acquainted with is in Wiedemann's *Lehre vom Galvanismus*, which, however, does not include a considerable number of researches published within the last few years.

Under certain circumstances, especially when currents of short duration are employed, the difference becomes very marked; so that on the whole "subsequent polarizations" have been recorded, for acidulated water for instance, of magnitude varying from something upwards of two or even three volts to something less than ·001 volt. With currents producing smaller values than 1·5 volt (measured immediately after rupture) visible evolution of gas at *both* poles does not seem to have ever been noticed. Recently Exner (Wied. *Annalen*, vi. p. 336, 1870) has shown that to cause visible evolution of gas from boiled-out distilled water, a "subsequent polarization" (measured immediately after rupture by a quadrant electrometer) of from 2·03 to 2·09 Daniell cells (from 2·2 to 2·3 volts) must be established; whilst if the water be faintly acidulated, a polarization of about 1·89 Daniell = 2·1 volts is sufficient. And in the same paper he has also shown that the polarization set up after the current is ruptured differs from the E.M.F. of the battery employed (and *à fortiori* from the counter E.M.F. set up during the passage of the current) only by quantities too small to measure accurately by a quadrant electrometer, when the battery E.M.F. does not exceed from 1·40 to 1·47 Daniell cell (1·54 to 1·61 volt) when larger platinum plates and boiled-out dilute acid are used, and from 1·94 to 2·09 Daniell cells (2·1 to 2·3 volts) with Wollaston's points (platinum wires coated with glass, so as only to expose a minute surface at the ends); whilst with stronger battery electromotive forces than these values the subsequent polarization always falls sensibly short of the battery E.M.F.

60. Various determinations have been made of the E.M.F. which a Grove's gas-battery can generate under various conditions. When the gases are oxygen and hydrogen, it has uniformly been found that the E.M.F. generated is less than 1·50 volt, the value representing the work done in the union of ordinary gaseous oxygen and hydrogen to form liquid water, which is the end result of the action taking place in such a cell when it generates a current. Recently Osgood Pierce (Wied. *Annalen*, viii. p. 98, 1879) has found numbers varying from ·766 to ·926 Daniell cell (·84 to 1·02 volt), according to the temperature, the nature of the liquid present, the purity of the oxygen, &c. *Cæteris paribus*, increasing

the temperatures lowers the E.M.F; Morley has recently shown (Proceedings Physical Society, ii. p. 212, 1878) that when a Grove gas-battery produces a current the E.M.F. is not constant, but is a function of the current produced, being the smaller the greater the current, *i. e.* the less the external resistance, and *vice versa.*

61. A clear coherent explanation of the differences in the numerical values of these quantities obtainable under various conditions, accounting quantitatively for them, and consistent with well-known dynamical principles, does not appear as yet to have been brought prominently forward; the following attempt in that direction is the result of a somewhat prolonged experimental investigation, some of the results of which are detailed subsequently.

Theorem.—Were it possible that the surface-action of the electrodes, the chemical action of substances dissolved in the fluid electrolysed, or of the electrode materials themselves, and other interfering causes (such as the accumulation of fluids of different densities round the electrodes) could be entirely eliminated, *the primary effect of electrolysis would be to break up the electrolyte into "nascent" products, the formation of which would correspond to a definite amount of work, and consequently to a definite E.M.F.*; but the physical attraction exerted by the electrodes upon the nascent products causes a certain proportion of them (variable with circumstances) to be converted *ab initio* into products, the formation of which from the "nascent" products is accompanied by a gain of energy (or evolution of heat). Similarly, under certain conditions the products of electrolysis are chemically acted upon by the electrodes, or by gases occluded upon their surfaces, substances dissolved in the fluid electrolysed, &c.; whilst, as the action proceeds, solutions of different densities accumulate round the electrodes, tending to set up an E.M.F. in virtue of their interdiffusion. All these circumstances modify the amount of work actually performed by the curent whilst causing electrolysis, in such a way that *the algebraic sum of the energy gained by these other actions is subtracted from the energy that would otherwise be required to break up the electrolyte into nascent products.*

This theorem may be put in the form of the following

equation.—Suppose that the quantity of total products of electrolysis at the negative electrode be called 1, and out of this amount let $1-n_1$ parts be evolved "nascent," whilst n_1 parts are so affected by the condensing or attractive action of the electrode as to be evolved *ab initio* not in the "nascent" condition, but in a more condensed form, viz. in the ordinary physical condition of the substance, if non-gaseous, but, if naturally gaseous, in the form of a more or less condensed form of gaseous matter (occluded gas, quasi-liquefied gas, or gas strongly attracted to the surface of the electrode). Let H_1 be the heat evolved per gramme-equivalent of product in its transformation from the "nascent" to the ordinary free condition, and let h_1 be the heat evolved in further condensing a gramme-equivalent of the substance to the more condensed form in which the fraction n_1 of total product is evolved. Similarly let n_2, H_2, and h_2 be the values corresponding respectively to n_1, H_1, and h_1, referring to the products at the + electrode taken as unity. Then the amount of energy to be subtracted from that corresponding to the decomposition into the nascent products due to the attractive action of the electrodes is given in terms of E.M.F. by the expression

$$\{n_1(H_1+h_1)+n_2(H_2+h_2)\}\chi J.$$

The energy corresponding to the work done in the decomposition into nascent products being expressed in terms of E.M.F. by E_l, let $\Sigma(\mathbf{H})$ represent the heat-evolution per gramme-equivalent of substance decomposed, due to the algebraic sum of the chemical actions taking place between the products and the electrodes, &c., and of the diffusive action of the differently constituted liquids surrounding the two electrodes; then the final E.M.F. corresponding to the work done in electrolysis will be

$$e=E_l-\{n_1(H_1+h_1)+n_2(H_2+h_2)+\Sigma(\mathbf{H})\}\chi J.$$

If now E_1 represent the E.M.F. corresponding to the work done in decomposing the electrolyte into the final products, supposing them to escape in the ordinary free condition,

$$E_1=E_l-(H_1+H_2)\chi J\ ;$$

whence

$$e=E_1+\{(1-n_1)H_1-n_1\,h_1+(1-n_2)H_2-n_2h_2-\Sigma(\mathbf{H})\}\chi J,$$

which may for shortness be written

$$e=\mathrm{E}_1+[\Sigma\{(1-n)\mathrm{H}\}-\Sigma(nh)-\Sigma(\mathbf{H})]\chi\mathrm{J}.$$

62. According to the particular values which the several terms in this expression may have, various values for e may be deduced. On examination it is found that all the apparently abnormal variations in the value of the counter E.M.F. set up during electrolysis, of the subsequent polarization, and of the closely allied E.M.F. produced by gas-batteries and analogous combinations may be satisfactorily accounted for by this expression *. Thus, for instance, suppose water to be electrolysed with platinum poles, so that no chemical action takes place between the electrodes and the products, whilst no suppression of hydrogen by the action of dissolved oxygen, or of hydrogen by dissolved oxygen takes place; then $\Sigma(\mathbf{H})=0$. If now the electrode be supposed to be destitute of adherent or occluded gases to commence with, and the current be very minute, the whole of the water decomposed will be transformed into hydrogen and oxygen in a highly condensed form, whence, since $n_1=1$ and $n_2=1$,

$$e=\mathrm{E}_1-(h_1+h_2)\chi\mathrm{J}=\mathrm{E}_1-\Sigma(h)\chi\mathrm{J}.$$

Under such conditions therefore *the water will be electrolysed by an* E.M.F. *less than* 1·50 *volt* (the value of E_1). Experiment shows in fact that when well-boiled water (either nearly pure or acidulated with sulphuric acid) is decomposed with recently ignited platinum electrodes, an E.M.F. scarcely appreciably greater than 0 will suffice to enable a current to pass, whence $(h_1+h_2)\chi\mathrm{J}$ must, under these conditions, nearly $=1{\cdot}50$ volt,

or h_1+h_2 must nearly $=34{,}100$ gramme-degrees;

that is, *the heats of condensation of oxygen and hydrogen by platinum &c. jointly may amount to almost as large a quantity as that developed by their union to form liquid water.*

That the work done in the condensation of a film of gas by attraction to or occlusion in a solid body is great relatively to the mass of gas condensed is well known. The Author, con-

* At the request of the Publication Committee of the Physical Society, the discussion of several particular cases of this theorem and of their bearing upon and explanation of various phenomena observed by previous experimenters is omitted.

jointly with Prof. W. C. Roberts, has shown (Chem. Soc. Journal, 1873, p. 112) that the specific heat of the portion of hydrogen first occluded by palladium is much greater than that of the later portions, the limiting values being near to 9 on the one side and 3·4 on the other—or values respectively representing a condensation to something approaching the liquid state (judged by analogy with liquid bromine, the product of the combining number and specific heat of which is near 9), and a condensation but little exceeding that due to ordinary atmospheric pressure. Presumably when a film of gas is attracted to the surface of a solid, the portions first attracted are very highly condensed, the next ones less so, and so on, a kind of atmosphere or aura surrounding the body being thus produced of density varying from the maximum amount of condensation to the minimum, *i. e.* the pressure of the surrounding atmosphere. The total quantity of gas thus condensed is not inconsiderable: thus an ordinary porcelain or, better still, a platinum crucible, if ignited and cooled in dry air, will weigh less by from one to several milligrammes, according to its size, if weighed immediately it is cold, and before the film or aura of condensed gas expelled by the heat is completely re-formed, than it will weigh if allowed to remain some time in the dry air, and weighed after the aura has been attracted to saturation. The inequality in the deviations from Boyle's law exhibited by gases under high pressures, but when still far removed from their condensing or from their critical points, has been considered by many physicists to be probably largely due to the difference in the attracting or aura-forming capacity exhibited by the tubes and measuring-vessels used, according as the nature of the gas varies. Not only gases, but also liquids, are attracted by solids, forming a layer or aura of highly condensed liquid adherent to the solid: Schliermacher has recently calculated (Dingler, *Pol. Journal*, pp. 224, 471; Chemical-Society Journal, Abstracts, 1880, p. 363) that this causes an appreciable error in the determinations of the weight of a unit volume of water hitherto made.

63. When water is electrolysed with non-oxidizable recently ignited electrodes (*e. g.* of platinum), the length of time which must elapse before the electrodes become saturated with gases will depend on circumstances, and amongst others on the fact

that the water will tend to take up oxygen at the + electrode and hydrogen at the − electrode, and the solutions thus produced will diffuse towards the opposite poles, thus tending to set up a double form of "electrolytic convection."

Suppose that a current pass through acidulated water, so that gases are slowly evolved; if by saturating with oxygen the water surrounding the − electrode the hydrogen is wholly reconverted into water, leaving out of sight the formation of liquids of differing densities round the two electrodes, and supposing that the + electrode and fluid surrounding it are saturated with oxygen, it will result that

$$\Sigma(\mathbf{H}) = E_1 + \{(1-n_1)H_1 - n_1 h_1\}\chi J$$

(the n_1, H_1, and h_1, referring to hydrogen), whence

$$e = \{(1-n_2)H_2 - n_2 h_2\}\chi J.$$

Now when $n_2 = 0$ this value is +, being $H_2\chi J$; but if $n_2 = 1$ it would become negative, $= -h_2\chi J$: for certain values of n_2 therefore (*i. e.* for certain rates of current-flow, Part IV.), the value of e whilst still + must be less than 1·50 volt; *i. e.* when "electrolytic convection" takes place, so that the hydrogen evolved by electrolysis is reoxidized as fast as generated, *electrolysis may be produced by means of a less E.M.F. than* 1·50 *volt.* Obviously the same result follows if the hydrogen be unoxidized, but the oxygen be reconverted into water by dissolved hydrogen; and the same may ensue if only a part of the hydrogen or oxygen is thus reconverted into water.

64. Again, when $\Sigma(\mathbf{H})$ is negligible compared with the other terms, and n_1 and n_2 are both small, the value of e may be greatly superior to E_1; for when n_1 and n_2 are both $=0$ and Σ (H) is negligible,

$$e = E_1 + (H_1 + H_2)\chi J = E_t.$$

Experiment shows that, *cæteris paribus*, the stronger the current the smaller are the values of n_1 and n_2; that is, e continually increases as the current increases, tending towards a limiting value in any given case (Crova, *Ann. Chim. et Phys.* lxviii. p. 413, 1868). Although at present the data for calculating accurately the limiting values of E_t for various substances are not extant, yet it is known that in the case of water E_t must

be upwards of 3 volts; for values of e above 3 volts have been observed: that is, the value of H_1+H_2 is greater than 34,100 gramme-degrees; or *the heat of transformation of the "nascent" products of electrolysis of water into gaseous oxygen and hydrogen jointly exceeds the heat developed by the combination of these gases at ordinary temperature and pressure to form liquid water.*

The theorem therefore accounts for all possible variations in the counter E.M.F. set up during electrolysis, between the minimum values (when the normally gaseous products of electrolysis are evolved not as free gases, but as condensed films of attracted or occluded gas, or when they are chemically acted upon by the electrodes or other substances in contact with them, *e. g.* during the so-called "electrolytic convection" of Hemholtz) and the limiting maximum reached with an indefinitely large current.

65. Before passing from this point it is worth noticing that the circumstance that the limiting value of E_t for water must lie above 3 volts shows that the first action of the current can be neither of the three following changes :—

(1) $2H_2O=H_2O_2+H_2$;

(2) $3H_2O=3H_2+O_3$;

(3) $\begin{cases} H_2O+H_2SO_4=H_2+H_2SO_5 \\ \text{or } H_2O+2H_2SO_4=H_2+H_4S_2O_9, \end{cases}$

forming respectively gaseous hydrogen and hydrogen dioxide, gaseous hydrogen and ozone, and gaseous hydrogen and the "persulphuric acid" of Berthelot; for that observer has shown (*Bulletin Soc. Chim. Paris*, 1876, xxvi. p. 56, and 1880, xxxiii. p. 246), that the amounts of heat absorbed by the addition of 8 grammes of oxygen to 9 of water to form hydrogen dioxide, to 16 of oxygen forming ozone, and to sulphuric acid forming persulphuric acid, are respectively 10,800, 14,800, and 13,800 gramme-degrees; so that the transformation of 8 grammes of ordinary oxygen into 8 of ozone would absorb $\frac{14,800}{3}=4933$ gramme-degrees, and the above three decompositions would absorb per gramme-equivalent (1 gramme of hydrogen evolved) respectively $34,100+10,800=44,900$, $34,100+4933=39,033$, and 34,100

+13,800=47,900 gramme-degrees, corresponding to the setting-up of counter electromotive forces amounting respectively to only 1·98, 1·72, and 2·11 volts, or far below the actual maximum. Even, therefore, if it be admitted that persulphuric acid is the body of which the oxygen that finally escapes is first produced as a constituent, it must be supposed that the hydrogen is evolved as an allotropic modification absorbing heat in its formation from ordinary gaseous hydrogen; whilst if this be admitted for hydrogen, it seems at least probable that the same is true for oxygen, and that the hydrogen dioxide, persulphuric acid, and ozone, found to be formed under certain conditions, are secondary products due to the reaction of the "nascent" oxygen on water or sulphuric acid, or to its "rearrangement" into ozone, just as the oxygen ultimately developed is due to a further rearrangement.

In accordance with the ordinarily received views as to the atomic and molecular constitution of matter, it would seem to result from the fact that the maximum counter E.M.F. set up during electrolysis of water exceeds 3 volts, that the first action of the current is to break up the water (and similarly for other electrolytes) into *free atoms* of the components, which atoms then rearrange themselves into molecules either as a secondary action or under the condensing action of the electrodes, or both; whence it would seem that *the sum of the heat of condensation of hydrogen atoms to molecules together with that of oxygen atoms to molecules exceeds that of the union of the hydrogen and oxygen atoms together to form molecules of liquid water.*

66. The phenomena connected with "subsequent polarization" (§ 58, footnote) are just as readily explained by the theorem as those relating to the counter E.M.F. set up whilst the current is passing. When visible decomposition has taken place for some time, so that the electrodes are surrounded respectively with a saturating aura of hydrogen and of oxygen, varying in density from the highest to the lowest possible value, and when, in addition, there are in the vicinity of the electrodes more or less of the "nascent" products of electrolysis, the counter E.M.F. set up during the passage of the current, and therefore representing the polarization at the

instant of rupture, is (§ 61)

$$e=E_1+[\Sigma\{(1-n)H\}-\Sigma(nh)-\Sigma(\mathbf{H})]\chi J.$$

After the lapse of a given interval of time (however small), more or less of the "nascent" products have spontaneously changed into the final products, viz. oxygen and hydrogen, thereby diminishing the value of $\Sigma\{(1-n)H\}$, and consequently lessening the value of e, the "polarization." Even after sufficient time has elapsed for the whole of the "nascent products" to have thus transformed themselves, the diffusion of water containing dissolved oxygen to the hydrogen electrode from the other, and of water containing dissolved hydrogen from the hydrogen electrode to the other, will still cause, by chemical action, a continual removal of portions of the aura of attracted gas round each electrode, thereby causing a continual increase in the mean value of $\Sigma(nh)$*, and hence a further diminution in the value of e; finally the polarization must become 0, when

$$\{\Sigma(nh)+\Sigma(\mathbf{H})\}\chi J=E_1=1{\cdot}50 \text{ volt.}$$

Experiments on the rate of diminution of the "subsequent polarization" and the circumstances influencing it are detailed later on (§ 69 *et seqq.*).

67. When an electrolytic cell (*e. g.* a voltameter), the electrodes of which are destitute of attracted films of gas or occluded gases, is connected with an electromotor and a cur-

* Gladstone and Tribe have shown (Chem.-Soc. Journ. Trans. 1878, p. 306) that hydrogen condensed by surface-attraction upon or occluded by certain solids (*e. g.* palladium, platinum, or carbon) exerts a much more energetic reducing action upon various substances than ordinary free hydrogen, the same result for palladium charged with occluded hydrogen (so-called hydrogenium) having been previously observed by Graham (Proc. Roy. Soc. xvii. p. 212, 1869). This result is not due to the condensed hydrogen being capable of evolving more heat by action on the substances in question than would be produced by the same quantity of free gaseous hydrogen, because the reverse is the case, the difference being the heat given out in condensing the hydrogen from the ordinary gaseous condition to the condensed form obtaining in the particular cases in question. The "catalytic" action of spongy platinum exemplified in Dobereiner's lamp, for instance, also illustrates this fact. The effect of the condensation, therefore, is analogous to that of increased temperature, causing chemical actions to take place that would not ensue (at least at any measurable rate) under other conditions, *i. e.* less condensation or lower temperature respectively.

rent of very short duration sent through it, if the amount of decomposition produced be so small that the hydrogen- and oxygen-development equivalent to the quantity of electricity passing are only small fractions respectively of the amount requisite to saturate the electrodes, no visible development of gas will ensue; the polarization at the instant of rupture of current will then be (§ 62)

$$e = E_1 - \Sigma(h)\chi J,$$

the value of h depending on the particular amounts of condensation to which the evolved products are condensed. On passing the current from the same electromotor for the same time again, a slightly less amount of current will flow; for the mean counter E.M.F. set up during this second interval of time will be somewhat greater than that during the first, whilst the total resistance in circuit is the same, whence the current (which $= \frac{\Sigma(E)-e}{\Sigma(R)+R}$, § 57) must lessen. Similarly, on passing the current again and again for equal intervals of time, quantities of electricity will pass in each interval, gradually diminishing in amount; whilst the "subsequent polarization" continually increases, the voltameter acting as a condenser, the capacity of which is simply measured by the power of the electrodes to condense upon their surfaces and occlude internally the products of electrolysis. On discharging a charged condenser by causing it to generate a regular succession of currents of equal but very short duration as to time, the quantity of electricity conveyed in each interval must at first be nearly the same, but will gradually diminish. These and various other analogous points in connexion with the behaviour of a voltameter as a condenser have recently been quantitatively studied by Herwig (Wied. *Ann.* ii. p. 601, and vi. p. 305), whose results are perfectly in accordance with the deductions from the general theorem above stated.

68. It is evident that the considerations that apply to the form of voltaic combination produced by the products of decomposition formed by the passage of a current through the decomposing-cell will equally apply if the same products of decomposition are introduced into the cell in other ways; so that if two platinum plates are exposed, the one to water

impregnated with ordinary oxygen gas, the other to water containing dissolved hydrogen, the two waters meeting, the attractive action of the plates will cause a more or less nearly saturated aura to be formed round each plate, and a difference of potential will be set up between the plates representing the work that would be gained by the combination of the condensed oxygen and hydrogen: in fact, the form of Grove's gas-battery thus produced will be identical in all respects with that developed when water is decomposed in a voltameter, except that in the latter case the polarization is more or less enhanced by the presence of the "nascent" products of electrolysis, at least until these have become wholly converted into the ultimate products. Such a gas-battery must therefore develop an E.M.F. expressed by the value of the formula

$$e=\mathrm{E}_1+[\Sigma\{(1-n)\mathrm{H}\}-\Sigma(nh)-\Sigma(\mathbf{H})]\chi\mathrm{J}$$

now obtaining; that is, since $n=1$,

$$e=\mathrm{E}_1-\{\Sigma(h)+\Sigma(\mathbf{H})\}\chi\mathrm{J},$$

or, since $\Sigma(\mathbf{H})$ must be extremely small, if not wholly negligible, practically,

$$e=\mathrm{E}_1-\Sigma(h)\chi\mathrm{J}.$$

Hence *the E.M.F. of a hydrogen and oxygen gas-battery cannot exceed* 1·50 *volt*, which experimentally is found to be the case. Any thing that affects the value of $\Sigma(h)\chi\mathrm{J}$ must affect the E.M.F. of a gas-battery; accordingly the E.M.F. is found to vary largely with the temperature, the nature of the plates, the fluid in which the gases are dissolved, the state of concentration of the gas-solutions therein, the presence of other gases, &c.; and in particular it is found to diminish with the strength of the current generated (Morley, *loc. cit. suprà*); for the more rapidly the films or auræ of gases attracted and those occluded are used up by chemical action, the less will be the mean densities of the auræ, and hence the greater will be $\Sigma(h)$ and the less the value of e.

Experiments on the Influence of dissolved Gases on the Rate of Fall of the Polarization existent after rupture of the original current (Subsequent Polarization).

69. It results from the general theorem above stated (§ 61), that the rate of fall of the "subsequent polarization" in any

given electrolytic cell (*e. g.* a voltameter) must be more rapid when the circumstances are such as to increase the numerical value of the term $\Sigma(\mathbf{H})$ than when the term is negligible; that is, the rate of fall must be a minimum (under any given conditions) when the fluids surrounding the electrodes (themselves unattacked by the products of electrolysis) have no chemical or physical action on these products, and when the electrodes have attracted and occluded as much of the products as they possibly can, but must be greater when these conditions are not fulfilled; so that in any ordinary voltameter, if the fluid surrounding the — electrode contain dissolved oxygen, the rate of fall must be greater than would be the case if no dissolved oxygen were present to act on the hydrogen aura; whilst, *cæteris paribus*, the larger the electrodes within certain limits, the less will probably be the effect of the oxygen dissolved in a limited amount of surrounding fluid on the hydrogen aura as a whole. Experiments on the rate of fall of "subsequent polarization" have been already made by Ayrton and Perry (Journ. Tel. Eng. v. p. 391, 1876), and the results expressed as curves; these observers, however, did not particularly examine the influence of varying amounts of dissolved air &c. on the rate of fall. On the other hand, Helmholtz, Fleming, and others have noticed that when water freed from dissolved air by boiling is electrolysed, the "subsequent polarization" diminishes less rapidly than when water containing dissolved air is employed.

The mode of observation adopted for the purpose of verifying the above deductions from the theorem was much the same as that used by Ayrton and Perry (*loc. cit.*). The electrodes of a given voltameter were connected with an electrometer, a suitable resistance being also in circuit, so that a current of known strength could be passed for any required length of time: to measure the current passing it was found convenient to employ a method based on Ohm's law, viz. reading off the difference of potential set up by the current between the ends of a known resistance by means of a quadrant-electrometer. This method, first, is independent of the errors (due to possible change of zero, horizontal magnetic component, &c.) of ordinary galvanometers, which cannot conveniently be verified without throwing them out of circuit or otherwise varying the

current passing by altering the total resistance in circuit, which is impracticable in experiments in which it is essential that the current should not sensibly vary during long periods of time,—and, secondly, enables the value of an extremely minute current to be determined with as much accuracy as that of a much stronger one, and even with greater accuracy; for whilst the current from a given electrometer is diminished by throwing more and more resistance into circuit, the difference of potential between the ends of the resistance thus thrown into circuit is not only not decreased but is even increased. For if e_1 be the E.M.F. of the electrometer, R_1 the resistance the difference of potential between the ends of which e_2 is measured, and R_2 the resistance of the rest of the circuit, the current passing

$$C = \frac{e_2}{R_1} = \frac{e_1}{R_1 + R_2},$$

whence

$$e_1 - e_2 = CR_2.$$

Hence, as C diminishes e_2 increases, and consequently a larger electrometer-deflection is obtained with a smaller current. Tolerably strong currents develop appreciable amounts of heat in the resistance-wire, thus increasing its resistance and introducing an error in deficiency in the current; so that the method is more particularly applicable for minute currents.

70. The difference of potential set up between the electrodes of a voltameter by the passage of a current C is $E = e + CR$, where e is the counter E.M.F. set up, and R the resistance of the voltameter (§ 57). If R do not exceed 100 ohms (100×10^9 C.G.S. units of resistance), and C do not exceed 0·0001 weber (0·00001 C.G.S. current-unit), the value of CR does not exceed $100 \times 10^9 \times 0{\cdot}00001 = 0{\cdot}01 \times 10^8 = 0{\cdot}01$ volt; whilst, whatever the value of C and R, the E.M.F. equal to the product CR is readily calculable. If now the difference of potential between the electrodes E be read off (in terms of the scale of the quadrant-electrometer) whilst the current is passing, by noticing the deflection of the spot of light from the zero (readings being taken on one side only), and the current be then interrupted, a motion backwards of the spot through a scale-length equivalent to CR will instantly ensue, and subsequently a con-

tinuous motion backwards as the value of e falls; if, however, CR be equivalent to considerably less than half a scale-division of the electrometer, the first sudden motion backwards will be entirely inappreciable. In the following experiments the electrometer was so arranged that 1 scale-division represented about 0·02 volt (readings being taken on one side only of the zero); and consequently as long as CR was less than 0·01 volt (*i. e.* as long as R did not exceed 100 ohms and C 0·0001 weber) the first sudden motion was less than 0·5 scale-division, and was consequently practically inappreciable.

(I.) Surface of each platinum electrode 3·2 square centims. Value of R=7·6 ohms; C=·000005 to ·0001 weber; so that CR was quite negligible; value of E at moment of rupture of current = 1·60 volt (average). The following numbers were obtained as the average of a number of concordant observations; the differences between the values obtained on repetition of an experiment were, as might be expected, much greater in the experiments of the A class than in the others.

Fall of E in volts.

Time in seconds since rupture of current.	A. Unboiled acid.	B. Acid well boiled and used as soon as cold.	C. Voltameter charged with acid saturated with hydrogen and oxygen at the two electrodes respectively.
5	·25	·20	·09
10	·33	·25	·13
15	·39	·32	·15
20	·43	·37	·17
30	·48	·45	·20
60	·59	·58	·26
120	·70	·70	·33
180	·75	·75	·35

(II.) Surface of each electrode 8·0 square centims. Value of R = 11·2 ohms, current ·000005 to ·0001 weber; so that CR was practically negligible. Average value of E at moment of rupture of current 1·80 volt.

Fall of E in volts.

Time in seconds.	A.	B.	C.
5	·26	·22	·19
10	·33	·27	·23
15	·39	·30	·25
20	·43	·32	·26
30	·48	·36	·28
60	·52	·38	·29
120	·56	·40	·295
180	·58	·41	·30

In precisely the same way analogous numbers were obtained in many other series of experiments, the details of which it is unnecessary to quote. Whether the electrodes were of gold, platinum, or carbon, whatever their size, and whatever the value of E, in all cases the general character of the numbers was the same as in these two examples; i. e. *the rate of fall with acid containing dissolved air was greater than that with acid freed from the greater part of the air dissolved by boiling; whilst this again was greater than that with acid from which the last traces of dissolved air had been removed* (from the fluid surrounding the hydrogen-pole) by the slow evolution of hydrogen therefrom, so as to saturate the fluid with hydrogen and remove the dissolved oxygen by "electrolytic convection." As the removal of the last traces of oxygen became more and more nearly effected, the rate of fall of polarization (for a given initial value) *gradually approached a minimum value*, beyond which it never sank, this minimum doubtless representing the rate of alteration produced in the auræ by diffusion from one electrode to the other.

71. The following experiments are specimens of a number of other analogous ones, all of which yielded the same general result, viz. that, other things being equal, *the rate of fall of polarization is less the larger the electrode surface.* The voltameters were precisely like those used in the above experiments, consisting of U-tubes with pieces of platinum-foil bent into cylinders and attached to platinum wires fused into glass tubes which served as mercury-cups—access of external air being prevented by closing each of the two open ends of the U-tubes with a doubly perforated cork (of india rubber, or paraffin),

the mercury-cup tube passing air-tight through one perforation and a delivery-tube (bent over and dipping under mercury or oil) through the other, so that evolved gas could escape without admission of air. The voltameters, being filled with boiled acid containing about 27 grammes of H_2SO_4 per 100 cubic centims., were then connected with a pair of Minotti cells, a large resistance being in circuit; so that a feeble current passed, evolving one or two cubic centims. of hydrogen per day. After some days (generally a week to a fortnight) the minimum rate of fall of polarization was arrived at; when this was the case, the electrodes were kept for another day at some particular difference of potential, arrived at by suitably altering the current passing and experimented with throughout, and a series of observations made; the electrodes were then again brought to the same difference of potential by passing the current again for some time, and another series of observations made; and so on. Finally, the following values were obtained from several such series of concordant observations, the experiments being alike in every respect save size of electrodes—the strength of the acid and the distance apart of the nearest portions of the electrodes being as nearly as possible the same throughout, and the U-tube being the same; so that diffusion must have gone on at as nearly as possible the same rate throughout. The numbers in the column headed "largest" were obtained with electrodes each exposing 27·5 square centims. surface; those in the columns headed "medium" and "smallest" with electrodes exposing respectively 3·2 and 0·2 square centims. of surface. In every case the value of CR was practically inappreciable.

(I.) Value of E on breaking circuit = 1·60 volt.

Fall of E in volts.

Time, in seconds.	Largest.	Medium.	Smallest.
5	·05	·09	·19
10	·08	·13	·27
20	·10	·17	·37
30	·12	·20	·46
60	·15	·26	·61
120	·19	·33	·75
180	·22	·35	·84

(II.) Value of E on breaking circuit $=1{\cdot}05$ volt.

5	less than ·01	·03	·17
10	·01	·04	·25
20	·02	·05	·31
30	·03	·06	·37
60	·04	·07	·44
120	·06	·09	·49
180	·07	·10	·52

It is evident from these numbers, specimens of many similar experiments, that the predictions from the general theorem mentioned in § 69 are completely verified by experiment. It may be noticed in passing that with the "largest" voltameter, when the value of E on breaking circuit was below 1 volt, the minimum rate of fall of polarization was so slow that no visible motion of the spot of light occurred even during many seconds, and with still lower values of E even after several minutes.

72. The following experiments are also of interest in connexion with this subject, as indicating how the rate of fall of polarization is affected not only by the removal of the auræ of gas round the electrodes by diffusion from one to the other of fluid containing dissolved gas, but also by the solution of the aura in the fluid itself (if not saturated with the gas constituting the aura), and also by the passage of gas into or out from the interior of the electrode, thus causing a diminution in the aura or *vice versâ*. Platinum- or gold-foil electrodes of various sizes being arranged in U-shaped voltameters like those just described, a gentle current was passed for some days, so as to saturate as far as possible, not only the liquids surrounding the electrodes with the gases respectively evolved on the electrodes, but also the interior of the foils with occluded gases. The electrodes were then rapidly removed, rinsed with recently boiled just cool acid to remove adherent solution of hydrogen or oxygen, and dipped into a U-tube containing the same recently boiled just cool acid. On connecting the two pieces of foil with a quadrant-electrometer a considerable potential difference was at once indicated. The two pieces of foil were then connected by a shortcircuiting wire for a short time (ten seconds usually); on removal of the wire, the foils being still connected with the electrometer, the spot of light moved regularly for a considerable time, indicating a gradual increase in the E.M.F.

of the voltaic arrangement thus produced, from 0 at the moment of removal of the shortcircuiting wire up to a maximum, which was maintained for some time, after which the E.M.F. gradually fell, precisely as in the experiments just described. It is evident that this development and rise of the E.M.F. set up was due to the formation and increase of an aura of gas round each electrode, the source of which was clearly the gas occluded internally in each respectively, the which gas now passed outwards by a reversal of the process by which it formerly passed inwards. The following three sets of readings (averages of fairly concordant repetitions of each experiment) will serve as specimens of a large number of analogous results; the numbers show the E.M.F. set up after the annexed time had elapsed:—

Voltameter used	"Largest."	"Largest."	"Medium."
Value of E on breaking circuit in the first instance (had been maintained for several days previously)	1·05 volt.	1·95 volt.	2·20 volts.
Time, after removal of shortcircuiting wire:—	volt.	volt.	volt.
5 seconds	·14	·35	·39
10 „	·19	·41	·44
15 „	·21	·43	·47
20 „	·23	·45	·50
30 „	·25	·47	·52
1 minute	·27	·52	·55
2 minutes	·28	·55	·58
3 „	·29	·57	·59
7 „	·29	·59	·60
10 „	·28	·59	·58
15 „	·28	·57	·55
30 „	·27	·53	·50
1 hour	·26	·49	·34
2 hours	·245	·44	·31
3 „	·235	·42	·29
4 „	·23	·40	·28

In these three cases the maximum E.M.F. was attained respectively after about 3–7, 7–10, and 7 minutes. The value of the maximum was much higher in the second case than in the first, indicating a much greater amount of gas occluded, as might be anticipated, since a much more rapid current flowed during the period before the electrodes were disconnected from the battery, the current being near to ·000001 and ·000020 weber during these periods in the first and

second cases respectively. Notwithstanding, however, that a still more rapid current (about ·000025) flowed in the third case, the maximum attained was scarcely higher than that in the second, because the smaller surface of the electrode caused the rate of loss of aura by solution in the unsaturated surrounding fluid and diffusion away of the solution thus formed to another part of the U-tube to be relatively larger in this case; consequently the rate of fall after the maximum had been reached was considerably more rapid.

73. A curious effect is sometimes produced by the gradual passage outwards from electrodes of occluded gases and the formation of an aura round each, thus virtually setting up a kind of Grove's gas battery. If the current passing through a voltameter be suddenly largely diminished (but not altogether interrupted) by diminishing the E.M.F. of the battery used, a considerable decrease is brought about in the counter E.M.F. set up in the voltameter; that is, the value of $e=E_1+[\Sigma\{(1-n)H\}-\Sigma(nh)-\Sigma(H)]\chi J$ diminishes. The passage outwards of occluded gas from the interior of the electrodes, however, tends to increase the aura round each electrode, and consequently to diminish $\Sigma(nh)$, and hence to increase e; and the result is that the voltameter behaves for a while like a more powerful opposed battery; so that *the current for a time passes in the opposite direction to that due to the primary electromotor*: of course this effect can only be produced when the E.M.F. of the primary electromotor (after the reduction in its E.M.F.) does not exceed some particular limit. If the experiment be modified by shortcircuiting the electrodes of the voltameter before again coupling them to the battery after reducing its E.M.F., the current will at first pass in the normal direction due to the battery; but as the occluded gases pass outwards from the interior of the electrodes and so form an aura round each, the current passing gradually diminishes in strength until it becomes *nil*, and finally passes in the opposite direction, just as it would have done at first had the voltameter not been shortcircuited. For example, a current of about ·00005 weber (capable of evolving about 0·5 cubic centim. of hydrogen per day) was passed for several days through a voltameter till the liquids surrounding the electrodes were saturated with oxygen and hydrogen respectively, for which

purpose a battery of two Minotti cells was used. One Minotti cell was then excluded from the circuit, a resistance of 50,000 ohms being included therein (the current being measured by determining the difference of potential set up between the ends of this resistance, as described in § 69), and the voltameter-plates shortcircuited for a few seconds. After removing the shortcircuiting wire, the current passed at a rapidly slackening rate in the direction due to the Minotti cell; but in a very few minutes it ceased to flow altogether, and then began to flow in the opposite direction. The shortcircuiting of the voltameter-plates was then repeated for two minutes, after which the current flowed in the normal direction at a gradually slackening rate: after one hour the current still flowed in the normal direction and had a value of +0·0000034 weber; but soon it became reduced to zero again, and then flowed in the reverse direction, having a value of −0·0000017 weber after two hours had elapsed since the second shortcircuiting. After twenty hours more the current was so small that its direction was inappreciable; but on removing the electrodes and igniting them and then replacing them, it flowed continuously in the normal direction. Similar results were obtained in many other analogous experiments.

The gradual setting-up again of an E.M.F. after shortcircuiting the electrodes of a voltameter has been already previously noticed by Ayrton and Perry, and the effect generally compared by them to the residual charge of a Leyden jar; they do not, however, appear to have observed the gradual extinction and reversal of the current just described.

74. It should further result from the general theory of electrolysis above stated, that if the electrodes of a voltameter are shortcircuited whilst still in contact with the fluid saturated with gases surrounding them, on removing the shortcircuiting wire the reproduction of an aura round each electrode will take place much more rapidly than will be the case were the electrodes removed and placed in fresh acid not saturated with gas, as in the experiments described in § 72; for in the former case the loss of aura produced by the passage outwards of occluded gas owing to solution in the liquid will be much smaller than that taking place in the latter case. That this is so the following numbers show, samples of numerous similar

observations made, each series of numbers being the average of several fairly accordant sets of determinations.

(I.) Platinum electrodes, exposing a surface of 27·4 square centims. each, kept at a difference of potential of 1·95 volt in each case for several days before the observations were made, the current passing being near to ·00002 weber. Shortcircuited for ten seconds.

Period since cessation of the shortcircuiting.	Electrodes not removed from the acid used whilst the original current passed.		Electrodes removed, rinsed, and placed in fresh acid (recently boiled and just cooled) before shortcircuiting.	
		volt.		volt.
During 1st minute.	Steady rise to	·86	Steady rise to	·52
2nd ,,	Further rise to	·95	Further rise to	·55
3rd ,,	,, ,, ,,	1·03	,, ,, ,,	·56
3rd–5th ,,	,, ,, ,,	1·11	,, ,, ,,	·58
5th–10th ,,	,, ,, ,,	1·24	Attained maximum	·59
10th–20th ,,	,, ,, ,,	1·26	Slight fall to	·55
20th–30th ,,	Attained maximum	1·27	Further fall to	·53
30th–60th ,,	Constant at	1·27	,, ,, ,,	·49
60th–120th ,,	Slight fall to	1·265	,, ,, ,,	·44
120th–180th ,,	,, ,, ,,	1·26	,, ,, ,,	·42
180th–240th ,,	,, ,, ,,	1·25	,, ,, ,,	·40

(II.) Electrodes exposing a surface of 3·2 square centims. each, kept at potential-difference of 2·20 volts, the current being near ·000025 weber. Shortcircuited for ten seconds.

Period since cessation of the shortcircuiting.	Electrodes not removed from the acid used whilst the original current passed.		Electrodes removed, rinsed, and placed in fresh acid (recently boiled and just cooled) before shortcircuiting.	
		volt.		volt.
During first 7 minutes.	Steady rise to	·60	Steady rise to	·60
7th–20th minute.	,, ,, ,,	·63	Slight fall to	·54
20th–30th ,,	Constant at	·63	Further fall to	·50
30th–60th ,,	Slight fall to	·61	,, ,, ,,	·34
60th–120th ,,	Further fall to	·57	,, ,, ,,	·31
120th–180th ,,	,, ,,	·51	,, ,, ,,	·29
180th–240th ,,	,, ,,	·49	,, ,, ,,	·28

75. The absolute mass of gas occluded by even moderately large foil electrodes is but minute; on Sprengelpumping at a red heat a platinum-foil electrode of about 160 square

centims. total surface (about 16 centims. long, and 5 broad), weighing four grammes, only barely recognizable traces of hydrogen were obtained, even when the electrode had been used for a long time and hydrogen copiously evolved from its surface during electrolysis. The presence of occluded hydrogen, however, can readily be observed by chemical tests, such as the reduction of ferric to ferrous salts, &c. One of the most sensitive was found to be that used by Osann (Pogg. *Ann.* xcv. pp. 311 and 315), viz. washing the electrode (in recently boiled just cool distilled water), and then immersing it in a clear brown-yellow solution of mixed ferric chloride and potassium ferricyanide. In a few minutes, according to the quantity of hydrogen occluded, a distinct blue precipitate forms on the surface of the platinum, due either to the conversion of ferri- into ferrocyanide, or to the reduction of ferric to ferrous chloride, or both together. In this way the presence of hydrogen can be distinguished in a platinum electrode (ignited in oxygen previously to use in the voltameter), even when no visible evolution of hydrogen gas from its surface has occurred, the E.M.F. of the battery used being too small to admit of a steady current passing at a rate more rapid than that representing the rate at which removal of the aura of condensed gas by the effects of diffusion (§ 70) takes place—for instance, when the battery-E.M.F. is not greater than 1·4 to 1·5 volt (Part iv. § 84 *et seq.*). In applying this test, however, too much reliance must not be placed on the formation of a blue precipitate after the lapse of a long time; for organic matters and reducing gases and vapours from the air are apt to be absorbed by the ferric ferrocyanide liquor, causing reduction, especially under the influence of light. Moreover, even platinum recently ignited and cooled in oxygen, when placed in the solution, becomes covered with a thin blue film after a considerable time (some hours or days), suggesting the possible reduction of ferricyanide to ferrocyanide with simultaneous production of platinocyanide. Gold acts in this way much more rapidly than platinum. In applying this test in the above-cited observations, check experiments were always made with a second piece of platinum foil of about the same size recently ignited: the blue deposit on the foil used as electrode was then found

to be notable or considerable when none at all was visible on the check piece.

76. From the general theory of electrolysis and the experiments above described, and the much more numerous analogous observations made but not described in detail for the sake of saving space, it results that the condition of the aura round each electrode of a voltameter that has been used for decomposing water at a given period since rupturing the original current is influenced by many circumstances. The aura round the — electrode, for example, has a particular mean density at the moment of breaking circuit, whilst that round the + electrode has some other mean density, the polarization then existent being governed by the proportions of "nascent" hydrogen and oxygen that were being evolved the instant previously and the mean densities of the auræ, *i. e.* by the values of n_1 and n_2 and h_1 and h_2 in the expression

$$e=\mathrm{E}_1+\{(1-n_1)\mathrm{H}_1-n_1h_1+(1-n_2)\mathrm{H}_2-n_2h_2-\Sigma(\mathbf{H})\}\chi\mathrm{J}$$

(§ 61). After the lapse of a given time, however, more or less of the "nascent" hydrogen and oxygen have rearranged themselves, and more or less of the original aura round each electrode has become reconverted into water by the effects of diffusion (bringing oxygen-containing fluid to the hydrogen-electrode and *vice versâ*); so that from these causes n_1 and n_2 have increased, each of these changes diminishing the value of e, the polarization. Simultaneously, however, each aura has been more or less reinforced by the passage outwards of occluded gas from within, each of these changes tending to increase e. Presumably the greater the extent to which the aura was wasted, so to speak, by diffusion, the more rapidly would this outward passage of occluded gases take place; so that finally the rate of fall of polarization is gradually retarded, first because as the "nascent" hydrogen and oxygen become expended by spontaneous rearrangement this source of fall of polarization regularly diminishes, and secondly because the greater the fall the more energetic is the restoring influence of the outward passage of the occluded gases, at least until the amount occluded becomes materially reduced in quantity. When the amount of fall is such that the rate of outward passage of occluded gases almost balances the rate of wasting of aura through diffusion, the rate of fall of polarization

becomes almost insensible, at any rate for periods of time not too prolonged. This point was reached in many of the experiments, in particular those with the "largest" voltameter and polarizations of values not exceeding a few tenths of a volt (§ 71). Ultimately, however, the occluded gases become exhausted and the auræ diminish to inappreciable quantities, the value of e diminishing to a quantity too small to measure. This result requires an enormous length of time to bring it about by the action of diffusion only; if, however, the voltameter-plates are united by an external connecting-wire, a current flows through that wire, and work is done at the expense of the energy stored up, so to speak, in the auræ and occluded gases of the electrodes. The capacity of the condenser virtually formed by the voltameter-plates simply means the quantity of electricity that can be made to flow in this way, and will approach the more nearly to the quantity of electricity that passed in forming the auræ and charging the electrodes with occluded gases the less has been the waste of auræ by diffusion &c. During the passage of the current, the auræ and the occluded gases are used up by chemical action, just as the zinc is in an ordinary cell; and as their quantity diminishes, the effective E.M.F. of the voltaic couple formed by the plates also diminishes.

If through leakage of the apparatus, or other causes, atmospheric air obtains access to the liquid surrounding the −electrode, the dissolved oxygen thence resulting will of course tend to reduce the aura of hydrogen by a chemical action of a kind akin to the "local action" of an ordinary voltaic element, *i. e.* not contributing to the work done by the current generated. In this case the rate of fall of the "subsequent polarization" (the electrode not being connected by a wire so as to produce a current) will be more or less enhanced above the rate due to diffusion only, as above described (§ 70); whilst if the electrodes are connected and a current is made to pass, the E.M.F. of the voltaic couple thus produced will diminish more rapidly than would be the case were no dissolved oxygen present in the liquid round the hydrogen-plate, just as the zinc of an ordinary cell wastes more rapidly when there is local action than it does when there is not, other things being equal.

PART IV.

[Plate VI.]

On the Validity of Faraday's Law as to the Proportionality between the Mass Electrolysed and the Quantity of Electricity passing; on the Numerical Relationships between the Counter Electromotive Force set up by weak Currents and the Rate of Flow of these Currents; and on the Conditions influencing these Relationships and the consequent Dependence of the E.M.F. of certain forms of Electromotors on the Currents generated by them.

77. The original experiments of Faraday and of many subsequent observers have amply established, for moderately strong currents, the truth of the proposition known as "Faraday's law," or as "Faraday's first law of electrolysis" (Part I. § 7), viz. that when a compound is electrolysed the weight of substance decomposed is sensibly proportionate to the quantity of electricity passing. Still, not only Faraday himself, but also subsequent experimenters have been led to doubt whether this law is rigorously true in all cases, *i. e.* whether it is not possible for very weak currents to pass through certain electrolytes without actually causing electrolysis, or at least without causing an amount of electrolysis precisely proportionate to the quantity of electricity passing. In other words, it has been held that "conduction without electrolysis" may occur in certain cases. On examining the experimental evidence in support of the doubt, however, it does not seem to be at all proved in the cases in which no electrolysis was apparent, even though a weak current passed, that electrolysis did not actually take place, the products being prevented from becoming visible owing either to secondary chemical changes, or other circumstances. More especially in the case of electrolysis of water is this deficiency of proof noticeable; for if the liquid electrolysed were in contact with air before ordinary electrolysis, the hydrogen evolved would necessarily be more or less completely suppressed by the oxidizing action of dissolved oxygen; whilst even in the case of experiments with boiled fluids, or fluids *in vacuo*, the impossibility of getting rid of the last traces of oxygen dissolved in the fluid or occluded in the

electrodes &c. would still affect the quantity of free hydrogen collected, as would also the power of the electrodes to occlude within their material, or to condense upon their surface, the hydrogen that would have appeared in the free state could these actions of the electrodes have been completely eliminated. Moreover it was shown long ago by Buff (*Ann. der Chem. und Pharm.* lxxxv. p. 1, and xciv. p. 15, 1853 and 1855) that currents in the ratio of $\frac{1}{R}, \frac{1}{R+r}, \frac{1}{R+2r}$, and $\frac{1}{R+4r}$, when passed through silver solutions deposited quantities of silver sensibly in the same ratio, even when the currents were so minute that the smallest of them only deposited 0·129 gramme of silver in 100 hours, and hence deposited $\frac{0{\cdot}129}{100\times 60\times 60}$ grammes per second, corresponding to a C.G.S. current of $\frac{0{\cdot}129}{360{,}000\times 0{\cdot}01163}=0{\cdot}0000308$, or to 0·000308 weber (1 weber = 0·1 C.G.S. current-unit), since 1 C.G.S. current-unit deposits 0·011363 gramme of silver (Part I. § 9). Similarly Buff found that currents capable of depositing from ·009 to ·113 gramme of silver per 100 hours (·000022 to ·00027 weber) evolved quantities of hydrogen usually only differing by less than ·05 cubic centim. from the quantities calculated from the current passing when air-free solutions of Glauber's salt, dilute sulphuric acid, or distilled water were electrolysed for from 4½ to 26 hours, so that from 0·11 to 1·09 cubic centim. were collected, the hydrogen pole being a Wollaston point; whilst a just visible evolution of hydrogen was noticeable from a Wollaston point with a yet smaller current, capable of depositing ·001 gramme of silver per 100 hours, and hence equal to ·0000024 weber. Whilst these experiments indicate that conduction without electrolysis did not take place to any appreciable extent during the electrolysis of the silver salt used, they are yet scarcely precise enough to establish with certainty the same point in the case of water, although they clearly point in that direction. Accordingly the following experiments were made with a view to supplementing Buff's work in this respect.

78. Voltameters were constructed like the one represented in Pl. VI. fig. 1. A U-tube, AB, was drawn out and cut off

in the middle of one of the limbs, and the drawn-out part passed through an indiarubber cork, C, smeared internally with melted rubber to make an air-tight joint. Over this cork (similarly smeared outside) was fixed a calibrated capillary tube widened into a sort of thistle-funnel or bell-mouth D, at the part into which the cork fitted; this tube was bent to a double right angle, so that the part used for measurement, EF, pointed downwards, the lower end passing through an indiarubber cork, H, into a second U-tube, G, the other end of which was closed by another rubber cork through which a stout glass rod, I, passed. The upper U-tube was provided with electrodes, K and L, of platinum-foil of measured size fixed to platinum wires fused through the glass (or sometimes, in the case of the longer limb, supported, as represented in the figure, by a loosely fitting cork in the open mouth of the tube), by means of a platinum wire sealed through a drawn-out glass tube, M, which, being filled with mercury, served as a mercury-cup. In order to fill the instrument, the corks supporting I, and also H, were loosened, and recently boiled, still hot, dilute sulphuric acid poured into the longer limb of the U-tube, AB. This acid rapidly filled this U-tube, and then passed over through the capillary tube, DEF, into the lower U-tube, G, also filling it. A certain amount of acid was allowed to run through the whole instrument, so as to rinse out the first portion poured in, which had probably absorbed air to some extent, after which the cork supporting I was firmly fixed, and then the cork H. If now the two electrodes were connected with a battery, evidently the gases evolved would arise, the one into the bell-mouth of this capillary tube, the other to the surface of the fluid in the longer limb, B, of the upper U-tube. By making K the — electrode, and by working the glass rod I up or down through the cork supporting it, the hydrogen evolved could either be drawn over into the measuring part EF, or forced back again into D; and in this way measurements of the gas contained in D could be readily made. When the quantity of gas collected became too large for measurement, it could be drawn completely over into the lower U-tube, G, so as to empty the bell and capillary tube of gas, by simply drawing out the rod I.

79. In order to saturate the acid in the two limbs A and B with hydrogen and oxygen respectively, as well as to do away with the sources of loss of hydrogen due to traces of residual air and occlusion by the electrode K, a weak current (about ·0000025 to ·000005 C.G.S. current-unit*, capable of evolving from about 0·2 to 0·5 cubic centim. of hydrogen per day) was passed through the apparatus for several days or even two or three weeks, the evolved hydrogen being from time to time drawn over into the lower U-tube G, and expelled by cautiously loosening the cork H for an instant or two. If during this time measurements were made of the quantity of hydrogen actually collected as compared with that calculated from the current passing (kept as nearly as possible uniform by suitably altering the resistance in circuit, and measured by determining the potential difference set up between the ends of that resistance, as described in Part III. § 69), it was found that a deficiency in the amount collected was always observed, but that that deficiency gradually decreased to a constant minimum. Moreover the period when this constant minimum was first reached was found to be precisely the period at which the rate of loss of polarization observed on breaking circuit reached its constant minimum (Part III. § 70); and it was also precisely the period when the counter E.M.F. set up by a given current with a given apparatus ceased to increase (§ 85). These coincidences, as well as *à priori* reasoning, leave no room for doubt that the cause of the residual constant discrepancy between the observed and calculated amounts of hydrogen is due to that cause of loss of hydrogen which cannot possibly be entirely removed, viz. the diffusion to the hydrogen plate of oxygen-containing liquid, and *vice versâ*; whilst the larger deficiencies at first noticed are due to this cause increased by the solution of hydrogen in the fluid, its occlusion by the electrode, and its oxidation by the last traces of unremoved air. That this is the true cause of the residual constant deficiency is moreover further indicated by the fact that the nearer together the electrodes and the wider the

* The currents used in the majority of the experiments described below being only small fractions of a weber, it is more convenient to measure them in millionths of a weber, or *microwebers*. One microweber = 0·000001 weber = ·0000001 C.G.S. current-unit; so that the above currents are respectively 25 and 50 microwebers.

bore of the U-tube, AB (that is, the more rapid the rate of diffusion), the greater, *cæteris paribus*, is the residual deficiency; whilst fluctuations of temperature, which would necessarily aid the diffusion of the gaseous solutions by setting up convection currents, considerably increase the deficiency. It might be supposed that perceptible errors in measurement of the hydrogen would be occasioned by the adherence to the electrode K of visible minute bubbles of gas; in practice, however, it was always found that gently tapping the U-tube AB caused such bubbles to rise so completely into the bell D, that no visible bubbles still adherent to K could be distinguished.

80. In order to determine quantitatively the amount of loss of hydrogen due to this unavoidable "diffusion discharge" (as for want of a better name it may be termed), a large number of observations were made with the different voltameters employed in the following way. Firstly, a current of 25 to 50 microwebers was passed until the residual deficiency became constant (for a given current); and then the current was gradually diminished at stages of two or three days apart, determinations of the hydrogen actually evolved per day, or per two or three days, being made. By-and-by a particular limiting current-value was arrived at, such that with the particular voltameter used no gas whatever was collected, no matter how long the current was allowed to pass, if the current-strength were below that limiting value; whilst if the current were above that amount, and provided the temperature was as nearly uniform as circumstances permitted, so that this effect of heat-convection currents was reduced to a minimum, a quantity of hydrogen was collected after a given time, the greater the larger the current-value. In this way the following limiting values were obtained with four voltameters, some of the particulars of the construction of which are annexed:—

Voltameter No. 1. Electrodes of platinum-foil bent into cylinders so as to be about concentric with the walls of the U-tube. Total surface of each electrode (reckoning both sides of the cylinder and including that of the piece of platinum wire connected with it to make contact) 27·5 square centims. Average bore of U-tube between the electrodes round the

bend =1·50 square centim. in section. Distance apart of centres of cylindrical electrodes =13·0 centims.

Limiting value of current, expressing the rate of diffusion discharge not seriously increased by effects of variation of temperature, =4·0 microwebers, capable of evolving about 0·04 cubic centim. of hydrogen at 0° and 760 millims. in 24 hours.

Voltameter No. 2. Similar electrodes, each exposing 8·0 square centims. of total surface. Centres of electrodes 8·0 centims apart. Average bore of tube 1·0 square centim. in section.

Limiting value of current 8·0 microwebers.

Voltameter No. 3. Electrodes of foil, each exposing 3·2 square centims. total surface. Centres of electrodes 6 centims. apart. Average bore 1·1 square centim.

Limiting current-value 5·0 microwebers.

Voltameter No. 4. Electrodes of platinum wire, eac exposing 0·19 square centim. of total surface. Distance apart 17 centims. Average bore of tube 0·08 square centim.

Limiting current-value 1·5 microweber.

Voltameters Nos. 1, 3, and 4 contained acid of which 100 cubic centims. contained 27·0 grammes of H_2SO_4. In the three cases the values of the limiting currents are evidently in the order of the facility with which diffusion would go on—the column of fluid between the electrodes being respectively 13, 6, and 17 centims. long, the first being widest and the last narrowest, whilst the current values are respectively 4·0, 5·0, and 1·5 microweber. The relatively larger value for the limiting current of voltameter No. 2 is explained by the fact that it contained a more dilute and consequently less viscid acid, 100 cubic centims. containing only 1·0 gramme of H_2SO_4.

The amount of current due to imperfect insulation of the voltameter &c. in these experiments was wholly inappreciable. On connecting the voltameter emptied of acid with a battery of two or three Minotti cells and a resistance of 100,000 ohms, no leakage-current at all could be detected; that is, the difference of potential between the ends of the resistance of 100,000 ohms was less than ·005 volt (half a scale-division of the quadrant-electrometer); so that the leakage-current was less than $\frac{\cdot 005 \times 10^8}{100{,}000 \times 10^9}$, *i. e.* less than 0·05 microweber, a cur-

rent which would require upwards of five years to evolve 1 cubic centim. of hydrogen from water.

81. The average current passing during any given experiment was determined as follows:—The voltameter having been arranged and the current turned on at a noted time, the difference of potential set up by the current passing between the ends of a known resistance (corrected when necessary for temperature) was determined by means of the quadrant-electrometer; and hence the current passing was known. During the first two or three hours the current usually diminished somewhat, owing to the increasing counter E.M.F. set up in the voltameter; but subsequently it remained sensibly steady, under suitable conditions as to battery-power, temperature, &c. By means of numerous observations the average currents passing in each of various successive periods of time were known; and hence the average current for the whole time was known. Thus, for example, the average currents in one experiment were as follows:—

Period.	Average current during period.
Commencement to 6 hours.	22·4 microwebers.
6 hours to 21 hours	22·1 „
21 „ 29 „	21·5 „

Hence the average current for the whole period is

$$\frac{6\times 22{\cdot}4+15\times 22{\cdot}1+8\times 21{\cdot}5}{29}=22{\cdot}03 \text{ microwebers.}$$

In standardizing the quadrant-electrometer, use was made either of a moderately newly constructed Clark's cell, or of one which had "run down" to a known extent as compared with a newly prepared cell*, the E.M.F. of a moderately new

* A large number of experiments made with Clark's cells showed that whilst the E.M.F. of comparatively newly prepared cells (*i. e.* a few days to some three months or so old) is sensibly constant *when suitable precautions are taken in the construction*, yet a gradual decrease in the E.M.F. begins to take place after a longer or shorter time and then goes on continuously. Experiments on the construction and the circumstances influencing the permanence of these cells and others of different kinds, are in progress, which will be described in a future paper; it may be noticed, however, that cells prepared with mercurous-sulphate paste, boiled in a Sprengel vacuum and enclosed in hermetically-sealed glass tubes free from air, appear to be preferable to cells prepared in accordance with Clark's directions with a sealing of melted paraffin-wax (Proc. Roy. Soc. xx. p. 444, 1872).

cell being taken from Clark's experiments to be

$$1{\cdot}457\{1-(t-15)\times 0{\cdot}0006\} \text{ volt}$$

at t° (*i. e.* the difference of potential set up by the cell between two poles of the same material being expressed by this amount). It hence results that if the value of the B.A. unit of resistance (on which the valuation of the E.M.F. of Clark's cell depends, Part II. § 54) be affected by any error, the values assigned to the current passing in the present experiments are also erroneous in the same ratio. In the majority of the experiments described below the difference in the calculated amount of hydrogen, according as the B.A. unit is assumed correct, or as being $\pm 0{\cdot}5$ or even ± 1 per cent. in error, is less than the error of measurement of the gas collected, together with the error due to the rate of "diffusion discharge" not being absolutely constantly equal to the values given above, owing to unavoidable fluctuations of temperature.

82. By comparing the quantity of gas collected after the passage of a known average current for a known time with the amount calculated from the current and time by the formula

$$w=(C-C')t\chi$$

(where w is the weight of the hydrogen, C the average current passing, C′ the current equivalent to the "diffusion discharge," and t the time in seconds), numbers were obtained according closely together: thus, for example, the observed quantities of hydrogen collected in the experiment cited in § 81 were as follows (voltameter No. 1 used):—

Period.	Milligramme of hydrogen.
Commencement to 6 hours.	0·004
6 hours to 21 hours.	0·0105
21 „ 29 „	0·0055
Total . .	0·0200

whilst the amount calculated from the formula is

$$(0{\cdot}000002203-0{\cdot}0000004)\times 29\times 60\times 60\times 0{\cdot}000105$$

gramme = 0·0198 milligramme;

or sensibly the calculated amount was actually obtained, the difference between the two quantities being only 0·0002 milligramme of hydrogen, representing about 0·002 cubic centim.

at 0° and 760 millims., an amount well within the experimental errors.

In precisely the same way the following numbers were obtained in a series of experiments with the same voltameter (No. 1). The currents are given in microwebers (1 microweber $=0{\cdot}0000001$, or 1×10^{-7} C.G.S. current-unit) in the first column, and the time in hours in the second; the third column gives the value of $Ct\chi$, and the fourth of $(C-C')t\chi$, the two sets of values being given in order that the amount of suppression of hydrogen due to "diffusion discharge" may be rendered manifest.

Average current, in microwebers.	Time, in hours.	Weight of hydrogen, in milligrammes.		
		Total calculated from quantity of electricity passing.	Previous amount, less that due to "diffusion discharge."	Observed amount.
380	30	·432	·428	·43
285	20	·216	·213	·21
200	23	·174	·170	·17
90	24	·082	·078	·076
80	42	·127	·121	·120
48	17	·030	·028	·027
47	42	·075	·069	·068
24	22	·020	·017	·017
22·0	29	·024	·020	·020
9·7	43	·016	·009	·009
4·7	48	·009	·001	·001
Less than 4·0	Various periods up to 192 hours.	——	nil.	nil.

Similarly, the following numbers were obtained with voltameter No. 2:—

750	1·25	·050	·049	·049
285	6·25	·067	·065	·063
191	5·25	·038	·036	·035
122	4	·018	·017	·016
113	21·25	·090	·084	·081
59	22·5	·050	·043	·041
34	23·5	·029	·022	·022
21·0	23	·018	·010	·010
17·0	55	·036	·018	·019
16·3	46	·030	·016	·016
Less than 8·0	Various periods up to 100 hours.	——	nil.	nil.

With voltameter No. 3 the following numbers were obtained:—

220	16	·133	·130	·130
65	24	·052	·048	·045
50	47	·089	·081	·080
6·3	41	·010	·003	·004
Less than 5·0	Various periods up to 240 hours.	—	nil.	nil.

And with voltameter No. 4 the following numbers:—

23·0	21	·018	·017	·017
20·0	24	·018	·017	·017
7·0	46	·012	·009	·009
Less than 1·5	Various periods up to 100 hours.	—	nil.	nil.

In nearly every instance the observed quantities of hydrogen and those calculated from the quantity of electricity passing, after subtracting the amounts due to "diffusion discharge," either coincide or do not differ by more than ·001 milligramme of hydrogen, or about 0·01 cubic centim., an amount of variation not outside the probable errors of measurement. In the few cases where the difference reaches ·002 or ·003 milligramme, the observed amount is always less than the calculated quantity, the cause being that the temperature could not be kept absolutely uniform, and consequently the loss of hydrogen by "diffusion discharge" is a little underestimated, the normal value of the rate of diffusion discharge being a little increased through the effects of heat-convection (§ 79). Some half dozen other experiments were made in which slightly greater differences were observed, always in the same direction, viz. deficiency in the amount of hydrogen collected; in these experiments the temperature fluctuated more than in those above cited, and hence the results are not quoted, being vitiated by the increased effect of heat-convection.

From these numbers the final conclusion may be fairly drawn, that *when water is electrolysed the mass decomposed is always proportionate to the quantity of electricity passing*, no matter how great may be the time it takes to pass, *i. e.* no matter how small is the actual current employed, thus comfirming and amplifying the results obtained by Buff

above quoted; so that the universal validity of Faraday's law may fairly be taken as being established. On the other hand, the recent experiments of Guthrie and Boys (Phil. Mag. [5] x. p. 328, Nov. 1880) show that a glass vessel filled with dilute sulphuric acid or other electrolyte, and suspended by a wire in a rotating magnetic field, is urged to a move by a force producing torsion in the wire varying as the product of the conductivity of the electrolyte into the relative speed of the magnets compared with that of the fluid set rotating whirlpool-fashion inside the glass vessel by induction; and it is supposed by the authors that, in this case, no electrolysis occurs, although currents circulate in the fluid. The absence of electrolysis, however, in these experiments, is not only unproved but is highly improbable. At any given instant any two opposite points on the inner surface of the glass containing-vessel in contact with the liquid will exhibit a greater or less difference of potential, and a current will flow between them through the liquid, the points on the glass surface acting as electrodes; after a half revolution the potentials of the two points are reversed, the current flowing in the opposite direction relatively to the points (but in the same direction relatively to the magnets); so that so far as these two points are concerned a series of alternating currents (or rather of currents going through a regular cycle increasing from 0 to a + maximum, decreasing to 0 and then to a − maximum, and then increasing again to 0, and so on) are set up, the effect of which is to eliminate the effects of "polarization" as completely as in Kohlrausch's method of determining conductivity by means of alternating currents, the products of electrolysis being reunited, so to speak, by the action of the reverse current before they have time to escape. Since the nett chemical action is nil, the work done by the currents appears solely as heat; but it does not therefore follow that electricity passes through the liquid without causing electrolysis, any more than in Kohlrausch's experiments.

Relationships between the Counter Electromotive Force set up during Electrolysis and the Rate of Flow of the Current passing.

83. It has often been noticed by previous observers that the so-called "polarization," or, more strictly, counter E.M.F.

(§ 57) set up during electrolysis, especially of acidulated water, by a given current, gradually rises until it becomes approximately constant. The cause of this is doubtless that so long as the fluid surrounding the hydrogen-electrode contains dissolved air, and so long as the electrodes and the fluids surrounding them are capable of further attracting, occluding, or dissolving the gases evolved in their proximity, the aura surrounding each electrode does not possess its normal average density; that is, the values of $\Sigma(nh)$ and $\Sigma(\mathbf{H})$, in the expression for the counter E.M.F. set up (Part III. § 61),

$$e=\mathrm{E}_1+[\Sigma\{(1-n)\mathrm{H}-\Sigma(nh)-\Sigma(\mathbf{H})]\chi\mathrm{J},$$

are greater at first than the values to which they finally subside.

For the same reason, if an electromotor of E.M.F not greater than 1 to 1·5 volt or so be connected with a voltameter containing diluted sulphuric acid (unboiled, or even if boiled), and provided with electrodes of non-oxidizable material, as is well known, a current flows at first, the strength of which gradually diminishes to a minute amount, whilst the so-called "polarization" of the voltameter increases until it differs from the E.M.F. of the electromotor by only a very minute quantity. With boiled acid, and especially in voltameters so constructed that neither the oxygen evolved at the + electrode nor the external air can reach the − electrode (saving by unavoidable diffusion), the rate of the diminution of the current is much greater than is the case when these conditions are not fulfilled. On trying experiments of this class, however, it was found that even with the most carefully constructed voltameters the current never became too small to measure, even after many weeks; it gradually subsided to a limiting value, below which it never sank (*i. e.* as long as the E.M.F. of the electromotor and the resistance of the circuit remained the same). No trace of gas, however, was evolved at either electrode; which was evidently due to the fact that, owing to "diffusion discharge," the hydrogen and oxygen evolved by the current became reconverted into water just as rapidly as they were generated by the current; so that the particular final steady current attained with any given apparatus measured the rate of diffusion discharge with that apparatus under the particular conditions of the experiment.

84. On comparing such results with different electromotors, it was at once perceived that when the resistance in circuit remained the same, the greater the E.M.F. of the electromotor the greater was the value of the final steady current that passed, although as long as the E.M.F. of the electromotor did not exceed a certain limiting value (different for each form of apparatus) no visible evolution of gas took place in any case ; *pari passu* with the increase in the strength of the current, the counter E.M.F. set up was found to increase; that is, the value of $e=E-CR$, where E is the difference of potential between the electrodes, C the current, and R the resistance of the column of fluid between the electrodes (Part III. § 57). Thus the following values were obtained with voltameter No. 1 above described (§ 80), and precisely analogous ones with the others.

Final steady current.	Value of e.
0·1 microweber.	0·140 volt.
0·13 ,,	0·297 ,,
0·24 ,,	0·468 ,,
0·5 ,,	0·615 ,,
0·8 ,,	0·929 ,,
1·2 ,,	1·395 ,,
2·3 microwebers	1·523 ,,
3·1 ,,	1·564 ,,
4·0 ,,	1·663 ,,

With this particular voltameter currents of greater magnitude than four microwebers caused an evolution of hydrogen (§ 80) ; with currents less than this amount none was obtained. Since the values of the counter electromotive forces set up by these currents were considerable, especially when the current was near the limiting value of four microwebers, it results that the hydrogen which combined with the oxygen diffusing to the − electrode, and the oxygen combining with the hydrogen that diffused to the + electrode, was the gas occluded within or condensed upon each electrode respectively, and not that produced by the electrolysis reoxidized *pari passu* with its formation ; for in the latter case the nett work done as electrolysis during the passage of this current would be *nil*, and hence e would $=0$. The action of the "diffusion

discharge" is therefore precisely like that of dissolved air present in the fluid electrolysed in the first instance (§ 76), comparable with the "local action" of an ordinary cell. In any given experiment the value of e will rise (the current remaining constant) until the rate of diminution of aura at each electrode due to this cause just balances the rate of increase through electrolysis. As this latter rises when the current is increased, so will the mean aura-density rise, and the amount of aura dissolved away from the electrode by the surrounding fluid in a given time, and consequently the rate of diffusion discharge, until the aura is at its maximum mean density, *i. e.* saturated, after which a further increase of the current simply causes free gases to escape. In this case the value of e is still found to increase with the current, obviously indicating that the values of the n's (*i. e.* of the fractions of hydrogen and oxygen not evolved in the nascent state *ab initio*) decrease as the current increases. Similarly, when the temperature falls the value of e rises (*cæteris paribus*) and *vice versâ*, indicating that a fall in temperature increases, and a rise decreases, the fractions of gases evolved "nascent" in the first instance.

The following experiments were then made with the view of investigating the effects produced in the value of e (that is, in the values of the n's) by altering certain of the conditions of electrolysis.

Effect of Alteration of the Size of the Electrodes.

85. It would seem *à priori* probable that whilst e increases with the current when the electrodes are the same, and decreases when the size of the electrodes is increased, the current remaining the same, it will remain constant if the current and size of electrode increase in the same ratio, so that the rate of flow of electricity per unit of electrode-surface (sometimes spoken of as the "density of the current") is constant. The following experiments show that this is so.

The voltameters used were mostly those described above (§ 78), or others of similar construction, only differing in that the measuring-tubes were replaced by ordinary fine tubes bent over and dipping under mercury or water, so as to allow of the evolved gas escaping without introduction of

air—a similar arrangement being applied at the limb containing the + electrode (as described in Part III. § 71). They were filled with boiled dilute sulphuric acid of such strength that 100 cubic centims. contained 27·0 grammes of H_2SO_4 (in other experiments different strengths of acid were employed), and then submitted to the action of a current of 25 to 50 microwebers for several days, or even weeks, until the rate of fall of the polarization noticed after breaking battery-contact became sensibly constant at its minimum value for the particular current passing (§ 70), at which time, as already stated (§ 79), the difference between the hydrogen actually collected and that calculated from the quantity of electricity passing also became reduced to the constant minimum. During the time that elapsed since first starting the experiment, observations of E, the difference of potential between the electrodes, were frequently made: the current C passing being also determined by observing the difference of potential set up between the ends of a known resistance also in circuit (Part III. § 69), and the resistance R of the voltameter being known from the dimensions of the column of liquid between the electrodes and its specific resistance (as determined by Kohlrausch and others), the value of $e = E - CR$, the counter E.M.F. set up, was known. It was invariably found that the value of e continually rose after first starting the experiment until it finally reached a constant maximum, the time when this maximum was reached being precisely coincident with the epoch when the minimum rate of fall of polarization and the minimum deficiency in hydrogen collected were attained.

Thus, for example, the following numbers were obtained with voltameter No. 1, when filled with acid containing 40·0 grammes of H_2SO_4 per 100 cubic centims., the values being calculated by interpolation from experiments in which the current was uniformly near to the value 1000 microwebers = 0·0001 C.G.S. current-unit.

Counter E.M.F. set up for a current of 1000 microwebers.

Freshly boiled acid just cool; values obtained during first few minutes of passage of current.	Values gradually increasing up to 1·965 volt.

After passage of a current of about 300 microwebers for two days, so as to evolve some 5 cubic centims. of gaseous hydrogen, and nearly saturate the voltameter-liquid with oxygen and hydrogen in the two limbs respectively.	Values gradually rising from 1·965 to 2·150 volts.
After another week's passage of a current of about 50 microwebers.	Values rising from 2·150 to 2·250 volts.
Constant maximum attained after a fortnight's passage of the current.	2·267 volts.

86. In precisely the same way analogous numbers were obtained with the same voltameter and different currents, or different strengths of acid, and similarly with the other voltameters. It was found that when the sources of loss of hydrogen other than diffusion discharge were wholly eliminated, the value of the counter E.M.F. set up with a given current not only remained constant as long as the current did not vary, but also was the same if the current was varied through a considerable length of time (whilst making other observations), and then brought back to the original amount. With feeble currents of strength not exceeding a small number of microwebers per square centimetre of electrode-surface, however, the value of e was found to be very sensitive to causes which would act on the equilibrium of the auræ surrounding the electrodes, especially to changes of temperature which would increase the normal effect of diffusion discharge by setting up heat-convection currents; so that the constant E.M.F. due to the original current was often not absolutely (but only approximately) arrived at until after the lapse of some hours. For this reason too, the counter E.M.F. observed was often less by 1 or even 2 or more per cent. in such cases when determined in the afternoon (in the warmest part of the day) than when determined the first thing in the morning—partly because the actual rise of temperature diminished its value, but more particularly because of the increased effect of heat-convection in affecting the auræ. In making the following determinations, therefore, the mode of procedure adopted was as follows :—The voltameter having been saturated with hydrogen

and oxygen in the two limbs respectively by a fortnight's passage of a current of some 50 or 100 microwebers, a particular current was adjusted to pass by applying a given battery (of Minotti, De la Rue and Müller, Leclanché, or other cells, as most convenient, but chiefly the three first), and introducing a given resistance into the circuit to measure the current with. The whole was then left to itself till the next day, when a number of careful observations of the current passing and the value of E were made at as early an hour as possible (usually about 9 o'clock), so that the effect of the heat-convection currents due to alteration of laboratory temperature should be a minimum. The particular temperature of the measuring resistance-coil (platinum-silver or German-silver wire) being known, its resistance in ohms R_1 was known; and the potential-difference in volts E′ being known by standardizing the scale of the electrometer by a Clark's cell, the current was known in C.G.S. units, being given by the formula $C=\frac{E' \times 10^8}{R_1 \times 10^9}$. The resistance of the voltameter, R, being known, the value of $e=E-CR$ was thus known (usually the term CR was negligible, or at least small compared with E). The current was then allowed to pass for 24 hours, and the observation repeated as early as possible in the day, and so on. Usually the results of consecutive days' measurements agreed extremely closely. When a sufficient number of daily determinations had been made, the resistance in circuit was altered so that a different current passed, and another series of determinations lasting over some days made, and so on. Sometimes after making various series of determinations of the relative values of C and e in this way, the value of C was brought back to nearly the same value as that possessed in observations of several days or weeks before. In such cases the values deduced in the second set of observations were sensibly the same as those formerly obtained; or at least they uniformly corresponded to points lying sensibly on the same mean curve, obtained by plotting the currents as abscissæ and the values of e as ordinates. Thus, for instance, the average of three closely accordant sets of consecutive morning readings with voltameter no. 1 (containing acid of which 100 cub. centims. contained 40·0 grammes H_2SO_4), made near the beginning of a

long series of determinations lasting over many weeks, and that of three other sets of accordant observations made near the end of the period, gave the following numbers—

Earlier series.		Later series.	
Current in micro-webers.	e in volts.	Current in micro-webers.	e in volts.
23·5	1·906	22·3	1·901
21·0	1·892	20·1	1·895
20·6	1·880	19·8	1·870
Average 21·7	1·893	20·7	1·889

thus giving the final average—Current = 21·2, e = 1·891.

Similarly with voltameter no. 4, containing acid of which 100 cubic centims. contained 27·0 grammes H_2SO_4, the averages of two similar series of daily observations, near the beginning and end respectively of a lengthened period of time during which the curve-values were being determined, were as follows :—

	Current in microwebers.	e in volts.
General average from early series.....	4·70	2·334
„ „ „ later „	4·85	2·337
Mean.....	4·77	2·3355

and so on in dozens of other analogous cases.

87. The following tables give the final averages deduced from four lengthened series of daily morning observations made with voltameters nos. 1, 2, 3, and 4 above mentioned (§ 80), containing acid of such strength that 100 cub. centims. contained 27·0 grammes of H_2SO_4. The average temperature of the different series of experiments was in each case not far from 18°, near to which temperature the specific resistance of dilute sulphuric acid was found to be as follows by Kohlrausch and Nippoldt (Pogg. *Ann.* cxxxviii. p. 379, 1869):—

Sp. gr. of acid.	Percentage of H_2SO_4.	H_2SO_4 per 100 cubic centimetres.	Specific resistance at 22°.	
			Mercury = 1.	Absolute (C.G.S. system).
		grammes.		
1·1431	20·2	23·1	14990	$1·424 \times 10^9$
1·2045	28·0	33·7	13133	$1·247 \times 10^9$

the numbers in the last column being deduced from those in the preceding one by taking the specific resistance of mercury on the C.G.S. system as being $0{\cdot}000095 \times 10^9$, *i. e.* 0·000095 ohm per column of 1 square centim. in section and 1 centim. long; whence, by interpolation, the specific resistance of acid containing 27·0 grammes H_2SO_4 per 100 cub. centims. is, at 22°, $1{\cdot}31 \times 10^9$. The numbers obtained by Kohlrausch (Pogg. *Ann.* Ergbd. viii. p. 1, and clix. p. 233, 1876) yield a slightly different value, about 12 per cent. higher.

Sp. gr. of acid.	Percentage of H_2SO_4.	H_2SO_4 per 100 cubic centimetres.	Conductivity at 18°. Mercury = 1.	Specific resistance at 18° (C.G.S. system).
		grammes.		
1·1414	20	22·8	·00006108	$1{\cdot}556 \times 10^9$
1·1807	25	29·5	·00006700	$1{\cdot}417 \times 10^9$

whence acid of 27·0 grammes per 100 cub. centims. would have a specific resistance of $1{\cdot}47 \times 10^9$ at 18°.

The value obtained by Paalzow for acid represented by H_2SO_4, 14 aq. (Pogg. *Ann.* cxxxvi. p. 489, 1869), was 14157 times the resistance of mercury at 19°. This acid contains 28·0 per cent. of H_2SO_4, representing 33·7 grammes per 100 cub. centims., possessing the specific resistance $1{\cdot}34 \times 10^9$, or about 8 per cent. higher than that found by Kohlrausch and Nippoldt.

On the whole the specific resistance of acid of the strength used, viz. 27 grammes per 100 cub. centims., may be taken as 1·4 ohm at 18°, whence the values of R for the four voltameters, calculated from the dimensions of the columns of fluid between the electrodes (§ 80), are :—

Voltameter No. 1. $\frac{13 \times 1{\cdot}4}{1{\cdot}5}$ ohms = 12·1 ohms.

„ No. 2. $\frac{8 \times 1{\cdot}4}{1{\cdot}0}$ „ = 11·2 „

„ No. 3. $\frac{6 \times 1{\cdot}4}{1{\cdot}1}$ „ = 7·6 „

„ No. 4. $\frac{17 \times 1{\cdot}4}{0{\cdot}08}$ „ = 298·0 „

Inasmuch as the value of the term CR is always small compared with E, in the expression $e = E - CR$, a much greater

r in the determination of R than that included in the above nates will produce no material effect on the accuracy of letermination of *e*.

Voltameter No. 1.

Surface of each electrode = 27·5 square centimetres.

ur-mi-ra.	Microwebers per square centim. of electrode surface.	Average value of E, in volts.	CR, in volts.	$e = E - CR$, in volts.	Remarks.
	0·06	1·480	.....	1·480	No visible evolution of gas.
	0·11	1·622	.....	1·622	,, ,,
	0·31	1·878	.....	1·878	Distinct evolution of gas.
	0·41	1·897	.....	1·897	,, ,,
	0·91	1·971	.....	1·971	,, ,,
	2·28	2·062	·001	2·061	,, ,,
	4·34	2·129	·001	2·128	,, ,,
	7·88	2·218	·003	2·215	,, ,,
	11·3	2·274	·004	2·270	,, ,,
	19·8	2·333	·007	2·326	,, ,,

Voltameter No. 2.

Surface of each electrode = 8·0 square centimetres.

	0·57	1·899	.....	1·899	No visible gas evolved
	1·42	2·012	.....	2·012	Gas visibly evolved.
	3·90	2·107	.....	2·107	,, ,,
	6·55	2·170	·001	2·169	,, ,,
	12·15	2·245	·001	2·244	,, ,,
	17·7	2·302	·002	2·300	,, ,,
	31·3	2·371	·003	2·368	,, ,,
	63·5	2·468	·006	2·462	,, ,,
	109·3	2·522	·010	2·512	,, ,,

Voltameter No. 3.

Surface of each electrode = 3·2 square centimetres.

2	0·03	0·892	.....	0·892	No gas evolved.
	1·34	1·700	.....	1·700	,, ,,
	2·00	1·996	.....	1·996	Slight evolution of gas.
	3·2	2·086	.....	2·086	Gas visibly evolved
	4·0	2·153	.....	2·153	,, ,,
	6·4	2·183	.....	2·183	,, ,,
	9·1	2·231	.....	2·231	,, ,,
	16·8	2·303	.....	2·303	,, ,,
	30·9	2·368	·001	2·367	,, ,,
	65·9	2·415	·002	2·413	,, ,,
	120·0	2·468	·003	2·465	,,

Voltameter No. 4.

Surface of each electrode = 0·19 square centimetre.

Mean Current, in microwebers.	Microwebers per square centim. of electrode surface.	Average value of E, in volts.	CR, in volts.	$e = E - CR$, in volts.	Remarks.
0·34	1·8	1·484	.....	1·484	No gas evolved.
0·9	4·7	2·032	.....	2·032	,, ,,
1·2	6·3	2·069	.....	2·069	,, ,,
2·8	14·7	2·275	·001	2·274	Slight evolution of gas.
3·4	17·8	2·291	·001	2·290	Distinct evolution of gas.
4·8	25·2	2·336	·001	2·335	,, ,,
6·1	32·1	2·367	·002	2·365	,, ,,
8·9	46·8	2·410	·003	2·407	,, ,,
16·6	87·4	2·496	·005	2·491	,, ,,
36·1	190·0	2·578	·011	2·567	,, ,,
67·1	353·0	2·629	·020	2·609	,, ,,
145·0	763·0	2·702	·044	2·658	,, ,,
248·0	1305·0	2·753	·074	2·679	,, ,,

88. Figs. 2 and 3 represent the curves thus obtained, the curves numbered 1, 2, 3, and 4 being those respectively obtained with the voltameters thus numbered; in fig. 2 the currents are plotted as abscissæ, and the values of e as ordinates. Evidently, from the nature of these curves, the following conclusions may be drawn :—

(1) As the current increases with a given voltameter the value of e increases, but at a less rapid rate; so that the curves are concave downwards.

(2) For a given current the value of e is the greater the smaller the electrode surface.

In fig. 3 the abscissæ are the quantities of electricity flowing per second per square centimetre of electrode surface*; evidently the four curves obtained with the four voltameters do not differ more from one another than may reasonably be ascribed to the not absolute uniformity of the conditions of

* Those determinations in which no hydrogen was evolved are omitted in every case, inasmuch as the effects of diffusion discharge are unequal for the different voltameters, and hence unequally reduce the value of e, leading to marked difference in the curves.

the surface of the electrodes (Nos. 1 and 2 being chiefly foil, No. 3 partly foil partly wire, and No. 4 wholly platinum wire), and to the unavoidable experimental errors; whence it may be concluded that

(3) for a given rate of flow of electricity per unit area of electrode, the value of e is independent of the size of the electrodes and of the current passing; *i. e.*, e remains the same when both electrode surface and current are altered in the same ratio.

Effect of Variation in the Strength of the dilute Acid used.

89. It has been concluded by previous experimenters that increasing or decreasing the strength of the dilute sulphuric acid electrolysed makes little or no difference in the value of e, and that, if any difference exist, it is in this direction—that the stronger acid gives, *cæteris paribus*, a smaller value for e, the effect being less nearly imperceptible with very weak solutions indeed, and being well marked when distilled water is compared with weak acid. The following experiments were made with the above-described voltameters, from which it results that as the strength of the acid is increased (from 0·2 to 40·0 grammes per 100 cubic centims.) a progressive diminution in the value of e ensues.

Acid containing 40·0 *grammes of* H_2SO_4 *per* 100 *cubic centims.*—Voltameter No. 1 was used: from Kohlrausch's numbers (Pogg. *Ann.* Ergbd. viii. p. 1, and clix. p. 233) it results that acid of 1·2207 sp. gr. containing 30 per cent. of H_2S_4O, and therefore containing in 100 cubic centims. 36·6 grammes of H_2SO_4, has a specific resistance of 1·37 ohm at 18°, whilst acid of sp. gr. 1·2625, containing 35 per cent., or 44·2 grammes per 100 cubic centims., has the specific resistance 1·40 ohm at 18°; whence evidently the specific resistance of acid of 40 grammes per 100 cubic centims. strength may be taken as 1·385 ohm at 18°, or close to 1·4 ohm, nearly the same as for acid of strength equal to 27·0 grammes per 100 cubic centims. (the minimum specific resistance being known to be at strength intermediate between 30 and 35 grammes per 100 cubic centims.); so that R is, as before, close to 12·1 ohms.

Current, in microwebers.	Microwebers per square centimetre of electrode surface.	E, in volts.	CR.	$e=E-CR.$
3·1	0·11	1·564	...	1·564
4·0	0·14	1·663	...	1·663
5·5	0·20	1·761	...	1·761
8·6	0·31	1·801	...	1·801
13·6	0·49	1·843	...	1·843
21·2	0·77	1·891	...	1·891
47·1	1·71	1·972	·001	1·971
76·3	2·77	2·034	·001	2·033
204·0	7·42	2·105	·002	2·103
281·0	10·2	2·143	·003	2·140
370·0	13·4	2·181	·005	2·176
679·0	24·7	2·223	·008	2·215
1140·0	41·4	2·303	·014	2·289

Acid containing 11·4 *grammes of* H_2SO_4 *per* 100 *cubic centims.*—Voltameter No. 3 employed. Value of R calculated from Kohlrausch's determination of sp. resistance* of sulphuric acid $=\frac{6\times 2\cdot5}{1\cdot1}=13\cdot6$ ohms.

Current.	Microwebers per square centimetre.	E.	CR.	$e=E-CR.$
6·8	2·1	2·125	...	2·125
9·8	3·1	2·156	...	2·156
12·3	4·0	2·218	...	2·218
16·9	5·3	2·256	...	2·256
29·0	9·0	2·297	...	2·297
45·8	14·3	2·340	·001	2·339
70·1	21·9	2·362	·001	2·361
109·9	34·4	2·420	·002	2·418
212·0	66·2	2·486	·003	2·483
306·6	94·8	2·529	·004	2·525

By interpolation from these values it is rendered evident that whilst with acid of 40 grammes per 100 cubic centims. the values of e for given currents were uniformly lower than those for the same currents obtained with the same voltameter and acid of 27·0 grammes per 100 cubic centims., the reverse holds with acid of 11·4 grammes per 100 cubic centims. The fol-

* Acid of 1·0673 sp. gravity containing 10 per cent. H_2SO_4, corresponding to 10·7 grammes per 100 cubic centims., gives sp. resistance at 18°=2·59 ohms; and acid of sp. gr. 1·1036 containing 15 per cent., corresponding to 16·6 grammes per 100 cubic centims., gives sp. resistance 1·87 ohm; whence, by interpolation, acid of 11·4 grammes per 100 cubic centims. has sp. resistance 2·50 ohms.

lowing figures show that this is *à fortiori* true for acid of 1·0 and of 0·192 gramme per 100 cubic centims.

Acid containing 1·0 *gramme* H_2SO_4 *per* 100 *cubic centims.*—Voltameter No. 2 used. Value of specific resistance of acid of 1 per cent. or sensibly 1 gramme per 100 cubic centims., 22·1 (Kohlrausch), whence $R=\frac{8\times 22\cdot 1}{1\cdot 0}=177$ ohms.

Current.	Microwebers per square centimetre.	E.	CR.	$e=E-CR.$
3·7	0·46	1·939	·001	1·938
10·0	1·25	2·165	·002	2·163
36·0	4·5	2·285	·007	2·278
124·0	15·5	2·415	·022	2·393
291·0	36·4	2·495	·052	2·443
363·0	45·4	2·527	·064	2·463
498·0	62·2	2·607	·088	2·519
754·0	94·2	2·751	·133	2·618

Voltameter No. 1 used. Value of $R=\frac{13\times 22\cdot 1}{1\cdot 5}=192$ ohms.

Current.	Microwebers per square centimetre.	E.	CR.	$e=E-CR.$
7·8	0·28	1·993	·002	1·991
17·3	0·63	2·114	·003	2·111
27·2	0·99	2·141	·005	2·136
48·1	1·75	2·193	·009	2·184
88·7	3·23	2·253	·017	2·236
149·3	5·43	2·294	·029	2·265
324·3	11·8	2·387	·063	2·324
442·0	16·1	2·431	·085	2·346

Just as with acid of 27·0 grammes per 100 cubic centims. (§ 91 and 92), the two curves obtained with acid of 1 gramme per 100 cubic centims. with voltameters Nos. 1 and 2 are sensibly identical.

Acid containing 0·192 *gramme per* 100 *cubic centims.*—Kohlrausch and Nippoldt found that the resistance of acid of 0·2 per cent. H_2SO_4 was 465100 times that of mercury at 22°, whence the specific resistance of acid of ·192 gramme per 100 cubic centims. may be taken as close to 45 ohms; so that with the voltameter used $R=\frac{6\times 45}{1\cdot 1}=245$ ohms, the plates being 6 centimetres apart, and the bore of the tube between them

averaging 1·1 square centimetre in section. The surface of each electrode with this voltameter was 3·5 square centimetres.

Current.	Microwebers per square centimetre.	E.	CR.	e=E−CR.
4·6	1·31	2·186	·001	2·185
15·2	4·34	2·300	·004	2·296
31·7	9·1	2·363	·008	2·351
60·3	17·2	2·468	·015	2·453
100·9	28·8	2·542	·025	2·517

Fig. 4 represents the curves obtained with these different strengths of acid, the abscissæ being in each case the current-flow per square centimetre of electrode surface: curve no. 1 is that obtained with acid of 40·0 grammes per 100 cubic centims.; the curve marked no. 2, that with acid of 11·4 grammes; those marked 3*a* and 3*b* the two with acid of 1·0 gramme per 100 cubic centims., obtained respectively with voltameters no. 2 and no 1; the curve marked 4 is that with acid of 0·192 gramme per 100 cubic centims.; whilst curve no. 5 is the average curve deduced for acid of 27·0 grammes per 100 cubic centims. from the preceding four sets of experiments. In all cases, *the weaker the acid the greater is the counter E.M.F. set up with a given rate of flow of electricity per unit area of electrode surface.*

Effect of Variation of the Material of the Electrode.

90. It is well known, from the experiments of previous observers, that the nature of the surface of the electrode considerably affects the value of the counter E.M.F. set up, and that in particular platinizing a platinum electrode largely decreases the counter E.M.F. set up by a given current. This effect, however, is partly due to the considerable increase in effective surface thereby occasioned. In order to see what effects would be produced by substituting polished gold or compact carbon for polished platinum, the following experiments were made:—The carbon electrodes were thin slabs about 1–2 millimetres thick, sawn from hard rods used for electric lights; they were were filed to a tolerably smooth

surface, and digested for some months with aqua regia—also boiled at intervals with hydrochloric, nitric, and dilute sulphuric acids. To make connection with the battery, the upper portions were wrapped round with platinum foil tightly tied on with platinum wire, connected to the glass mercury-cup supporting the electrodes; the whole of the platinum foil and wire was then covered with gutta percha, so that only carbon was exposed to the liquid in the voltameter. To make sure that as little as possible of metals &c. capable of being acted on by nascent electrolytic oxygen was present, they were used as + electrodes for several days in the electrolysis of dilute H_2SO_4, such a current being employed as to keep a continuous evolution of gas at the rate of some 50 to 100 cubic centims. of hydrogen per day. The superficial area of each electrode (measured by scale and compasses, and making no allowance for increase of surface due to the carbon being slightly pitted and not smooth) was 3·9 square centimetres.

The gold electrodes were similarly mounted, a platinum wire being fused to them, and the surface of the platinum covered with gutta percha, so that only gold was exposed to the liquid in the voltameter. Surface of each electrode = 17·0 square centimetres.

Values obtained with Acid containing 27 grammes per 100 cubic centims.

Gold Electrodes.

The distance apart of the centres of the electrodes was 15 centimetres, and the bore of the tube between them 1·1 square centimetre; so that $R = \frac{15 \times 1{\cdot}4}{1{\cdot}1} = 19{\cdot}1$ ohms.

Current, in microwebers.	Microwebers per square centimetre of electrode surface.	E, in volts.	CR.	$e = E - CR$.
9·8	0·58	2·139	...	2·139
14·7	0·86	2·312	...	2·312
34·0	2·00	2·407	·001	2·406
55·7	3·27	2·452	·001	2·451
156·9	9·23	2·515	·003	2·512
364·0	21·4	2·627	·007	2·620
668·6	39·3	2·701	·013	2·688

Carbon Electrodes.

The distance apart of the centres of the electrodes was 18 centimetres, and the bore of the tube 1·5 square centimetre; so that $R=\frac{18\times 1\cdot 4}{1\cdot 5}=16\cdot 8$ ohms.

Current, in microwebers.	Microwebers per square centimetre of electrode surface.	E, in volts.	CR.	e=E−CR.
6·7	1·7	1·446	...	1·446
8·1	2·1	1·460	...	1·460
10·9	2·7	1·504	...	1·504
16·7	4·3	1·583	...	1·583
32·2	8·3	1·662	·001	1·661
103·3	26·5	1·761	·002	1·759
135·8	34·8	1·782	·002	1·780
238·0	61·0	1·829	·004	1·825

Values obtained with Acid containing 1 *gramme of* H_2SO_4 *per* 100 *cubic centims.*

Gold Electrodes.

R in this case $=\frac{15\cdot 0\times 22\cdot 1}{1\cdot 1}=301$ ohms.

Current, in microwebers.	Microwebers per square centimetre of electrode surface.	E, in volts.	CR.	e=E−CR.
7·9	0·46	2·211	·002	2·209
27·8	1·63	2·401	·008	2·393
68·1	4·01	2·483	·020	2·463
130·0	7·65	2·562	·039	2·523
288·0	16·9	2·659	·086	2·573
496·0	29·2	2·775	·149	2·626

Carbon Electrodes.

R now $=\frac{18\cdot 0\times 22\cdot 1}{1\cdot 5}=265$ ohms.

Current, in microwebers.	Microwebers per square centimetre of electrode surface.	E, in volts.	CR.	e=E−CR.
5·6	1·4	1·500	·001	1·499
13·7	3·5	1·614	·004	1·610
25·2	6·4	1·701	·007	1·694
55·4	14·2	1·763	·015	1·748
85·1	21·8	1·823	·023	1·800
248·0	63·5	1·938	·067	1·871

Fig. 5 (Pl. VI.) represents the four curves thus obtained,—those marked 1 and 3 being the curves obtained with acid of 27·0 grammes per 100 cubic centims., and with carbon and gold electrodes respectively; and those marked 4 and 6 the curves obtained with acid of 1·0 gramme per 100 cubic centims., with carbon and gold electrodes respectively. The other two curves traced, marked 2 and 5, are put in for comparison, being respectively the mean curves obtained as above described with acid of 27·0 and 1·0 grammes per 100 cubic centims. with platinum electrodes. In each case the weaker acid gives the higher counter E.M.F. for a given rate of flow of electricity per square centimetre of electrode surface; but the effect produced by the variation in the strength of the acid is small compared with that produced by substituting platinum for carbon, or gold for platinum *.

It should be noticed, however, that it is highly probable that the counter E.M.F. observed with the carbon electrodes is somewhat diminished, at any rate for the smaller currents, by the circumstance that electrolytic "nascent" oxygen is capable of attacking carbon, forming CO and CO_2 (Beetz, Wied. *Annalen*, 1878 [2] v. p. 1; also Phil. Mag. 1879 [5] vii. p. 1); the effect of this would of course be to diminish e by a quantity equivalent to the heat evolved in the oxidation of the carbon (reckoned per gramme-equivalent of water decomposed). With currents of the minuteness of only a few microwebers it was not found practicable to prove directly the formation either of CO or CO_2; but the circumstance that the observed values for e fell slightly below 1·50 volt with the voltameter containing acid of 27 grammes per 100 cubic centims., and with currents of from 5 to 10 microwebers, or slightly above the current equivalent to the "diffusion discharge" found with the same voltameter substituting platinum electrodes for carbon ones (viz. close to 4·0 microwebers), together with the circumstance that with platinum and gold electrodes the value of e was never below 1·5 volt when the

* The two carbon curves lie a little below their true positions, owing to the effective area of the carbons being a little greater than their superficial measurement, on account of the unavoidable absence of perfect smoothness and slight pitting of the surface. The true area, however, exceeds that measured by only a small amount, the carbon surface having been filed and ground so that the surface was as nearly smooth as it could be made.

current exceeded that equivalent to the "diffusion discharge," would seem to indicate that the values of e for these currents found for the carbon electrodes were actually slightly below the values that would have been found had no oxidation of the electrode taken place.

Experiments with Oxidizable Electrodes.

91. Suppose that dilute sulphuric acid is electrolysed with copper electrodes so that a gramme-equivalent of copper sulphate is formed at the + electrode for one of hydrogen evolved at the − electrode. In accordance with the general theorem (§ 61),

$$e=\mathrm{E}_1+[\Sigma\{(1-n)\mathrm{H}\}-\Sigma(nh)-\Sigma(\mathbf{H})]\chi\mathrm{J},$$

the value of e will be

$$e=\mathrm{E}_1+\{(1-n_1)\mathrm{H}_1-n_1h_1-\mathrm{H}_3\}\chi\mathrm{J},$$

where H_3 is the heat evolved during the production of a gramme-equivalent of copper sulphate from copper, ordinary free oxygen, and dilute sulphuric acid; for in this case $\Sigma(\mathbf{H})$ is equal to $\mathrm{H}_3+(1-n_2)\mathrm{H}_2-n_2h_2$ (the n_2, h_2, and H_2 referring to oxygen, and n_1, h_1, and H_1 to hydrogen), the diffusion effect of the copper sulphate solution accumulating round the + electrode being left out of sight.

Writing E_3 for $\mathrm{H}_3\chi\mathrm{J}$,

$$e=\mathrm{E}_1-\mathrm{E}_3+\{(1-n_1)\mathrm{H}_1-n_1h_1\}\chi\mathrm{J}.$$

Of course, if some other metal be used instead of copper, *e. g.* zinc, the same formula will apply, only the value of E_3 will be different.

If, instead of dilute sulphuric acid, a metallic salt, *e. g.* zinc or copper sulphate, be electrolysed, the same formula will hold, E_1 now representing the E.M.F. corresponding to the work done in decomposing the salt electrolysed into oxygen, metal, and dilute sulphuric acid, and E_3, as before, being the E.M.F. representing the work gained in synthesizing the salt produced by the solution of the + electrode from metal, oxygen, and dilute sulphuric acid; since $h_1=0$ when a solid metal is produced,

$$e=\mathrm{E}_1-\mathrm{E}_3+(1-n_1)\mathrm{H}_1\chi\mathrm{J}.$$

Taking into account the diffusive effect due to the strengthening of the metallic salt-solution round the + electrode and

its weakening round the — electrode [which, according to the results of Moser (Wied. *Annalen*, iii. p. 216), H. F. Weber (Phil. Mag. [5] viii. pp. 487 and 523), and Helmholtz (Wied. *Annalen*, iii. p. 201), may amount to at least some few hundredths of a volt under certain circumstances], this formula becomes

$$e=\mathrm{E}_1-\mathrm{E}_3+\{(1-n_1)\mathrm{H}_1+h'\}\chi\mathrm{J},$$

where h' is the heat corresponding to the diffusive effect of the concentrated and weak solutions per gramme-equivalent of electrolyte decomposed; h' is of + sign, since the results of the above experimenters show that the effect of the different densities of the solutions round the two electrodes is to cause a current to flow through the fluid from the weaker to the stronger solution, *i. e.* from the — to the + electrode *, or in the opposite direction to the current producing electrolysis.

If, then, dilute sulphuric acid, for instance, be decomposed by means of oxidizable electrodes, say of copper, the value of e will, under any given condition, be given by the formula

$$e=\{h'+h''+(1-n_1)\mathrm{H}_1-n_1h_1\}\chi\mathrm{J},$$

where $h''\chi\mathrm{J}=\mathrm{E}_1-\mathrm{E}_3$.

The same formula will also apply when a metallic salt is decomposed, $h''\chi\mathrm{J}$ still representing $\mathrm{E}_1-\mathrm{E}_3$, whatever values these two quantities may happen to possess. If the metallic salt decomposed contain the same metal as that dissolved from the + electrode, E_1 will approximately $=\mathrm{E}_3$, and h'' will nearly $=0$. Since, however, the physical condition of the deposited and dissolved metal will rarely, if ever, be identical, E_1 will not exactly $=\mathrm{E}_3$; h'' will represent the heat that would be evolved in the transformation of a gramme-equivalent of deposited metal into the physical condition of the dissolved electrode.

Since $h_1=0$ when a solid is deposited, the formula simplifies to this,

$$e=\{h'+h''+(1-n_1)\mathrm{H}_1\}\chi\mathrm{J}.$$

* Presumably this is only the case when heat is *developed* by the mixture of the strong and weak solutions; were heat *absorbed* during the intermixture, probably the current would be reversed in direction; for in that case the expenditure of work in order to effect electrolysis would be less instead of greater when the strong and weak solutions accumulated round the electrodes than it would be did diffusion and intermixture take place instantaneously.

So-called non-polarizable electrodes are, strictly speaking, misnomers ; they are only cases where the value of e is very small, owing to the particular conditions of the experiment rendering $(1-n_1)H_1+h'+h''$ but little greater than 0.

If the value of n_1 decreases as the current increases, when it refers to a metal deposited, as appears to be the case when it refers to hydrogen, from the above described experiments it results that the value of e will continually increase with the current, if the conditions of the experiment are such that h' and h'' remain constant (or if they are negligible).

92. *Decomposition of Acidulated Water with Copper Electrodes.*—In order to examine these points experimentally, known currents were passed through a U-voltameter filled with well-boiled, just cooled, dilute sulphuric acid containing 11·5 grammes of H_2SO_4 per 100 cubic centims., and fitted with copper electrodes each exposing a surface of 8·5 square centimetres. After allowing a current of some 50 to 100 microwebers to pass for two or three days the values of e became approximately steady ; the following numbers were obtained, the electrodes being 13 centimetres apart and the bore of the U-tube between them 1·09 square centimetre, so that the value of $R=\frac{13\times 2\cdot 5}{1\cdot 09}=30$ ohms, 2·5 ohms being (as calculated in § 89, footnote) the specific resistance of sulphuric acid of 11·4 grammes per 100 cubic centims. The values of E are all probably a little underestimated, because it was found impossible to allow a current of 25 to 50 microwebers to pass for a fortnight, so as completely to saturate the acid round the — electrode and the electrode itself with hydrogen, and get rid of the last traces of dissolved oxygen, as was done with platinum, carbon, or gold electrodes; for before a fortnight had elapsed, the copper dissolved from the + electrode and converted into copper sulphate had diffused to the other electrode and became partly re-deposited there (at least this phenomenon was observable in less than a fortnight when a polished platinum plate was used instead of a copper one for the — electrode). Probably this source of error affects all the observations about equally, and is but slight, since sensibly the same values of E were observed for a given current whether the observations were made on the 4th or on the 9th day.

Current, in microwebers.	Microweber per square centimetre of electrode surface.	E, in volts.	CR.	e=E−CR.
9·7	1·14	·523	...	·523
20·1	2·34	·548	·001	·547
49·8	4·23	·586	·001	·585
77·1	9·06	·600	·002	·598
108·7	12·4	·616	·003	·613
174·7	20·5	·669	·005	·664
226·0	26·6	·685	·007	·678
378·0	44·5	·720	·011	·709

These numbers clearly show that the values of $h'+(1-n_1)H_1-n_1h_1$ for currents of not less than 1·14 microweber per square centimetre of electrode surface are positive, and increase as the current increases; for h'' cannot exceed 0·4 volt, and the sum of h'' and $h'+(1-n_1)H_1-n_1h_1$ is uniformly greater than this. [That h'' is not $>0·4$ volt results from the valuations of E_s cited in Part I. § 21 and 22, deduced from the experiments of Favre, Julius Thomsen, and Raoult, which varied between 1·162 and 1·321, being uniformly above 1·1 volt, so that, as $E_1=1·50$ volt (Part II.), $h''=E_1-E_s$ cannot exceed 0·4 volt.] This increase is mainly due to the decrease in value of n_1 as the current increases; for on altering the current-strength to some value previously experimented with, the value of e always immediately altered to something very close to the value it previously was found to possess for the altered current, which could not have been the case had the increase in value of e found for a stronger current been simply due to the increase in the value of h' owing to the accumulation of copper sulphate solution round the + electrode.

Very little difference in the value of E was noticed when gold was substituted for copper as the negative electrode (the dimensions and the positive electrode remaining unchanged), the curve deduced by plotting the values of E−CR as ordinates and the rates of flow per square centimetre as abscissæ being nearly, though not quite, the same whether the − plate were copper or gold; what little difference did exist was of such a nature that the gold − electrode curve lay slightly above the copper one. On substituting platinum for

copper, the curve was very distinctly depressed; *i. e.* the values of E − CR for a given rate of flow and a constant copper positive electrode were smaller with a platinum electrode than with a copper one, and smaller with a copper one than with a gold one. Whether the values thus registered by the aid of the quadrant-electrometer are strictly comparable, or whether they are complicated by a difference of contact action taking place between the electrode and the brass quadrant of the electrometer (by means of the connecting-wire), is, however, open to discussion *. Admitting that the contact action does not materially affect the values obtained, the numbers found with the gold, copper, and platinum — electrodes would indicate that the value of n_1 is greater with platinum than with copper and greater with copper than with gold; *i. e.* the "condensing" actions of the three metals for "nascent" hydrogen lie in the order, platinum greatest, then copper, and lastly gold. As regards platinum and gold, this is precisely the conclusion to be drawn from the experiments described in § 90.

Experiments bearing further on the phenomena observed when the electrodes are not of the same material, will be considered in a future paper.

93. *Decomposition of Copper Sulphate with Copper Electrodes, and of Zinc Sulphate with Zinc Electrodes.*—The voltameters used consisted simply of U-tubes filled with the hot, just boiled, solution of zinc or copper sulphate employed, and then closed by india-rubber stoppers through which passed glass tubes with platinum wires through the drawn-out ends, so as to make mercury-cups, and keep the solution from access

* It is manifest that, whatever may be the nature of the contact actions between two dissimilar metals &c., and however this may affect the determination of the true difference of potential between two dissimilar plates connected respectively with the two quadrants of an electrometer, such actions have no influence at all on the result when the two metals are the same; so that whilst the mercury in a mercury-cup and two thick copper wires dipping into it may differ in potential, yet the two wires will be at the same potential, *i. e.* just away from the mercurial surface; and the difference of potential between the two quadrants of an electrometer is the same as that between the two plates of a voltameter &c. respectively connected with them when these plates are of the same material, *e. g.* platinum, although the intermediate connecting-wires and plates themselves may differ in their absolute potentials from the quadrant-potentials.

of air; to the platinum wires were soldered the electrodes, consisting of well-brightened strips of metal of known size, the solderings and platinum wire being covered over with gutta percha. By introducing a known resistance into the circuit, composed of voltameter and electromotor (one or more De la Rue, or other analogous cells), the current could be regulated and measured, and hence the value of $e=E-CR$ determined. In this way the following numbers were obtained. With the copper-sulphate voltameter (which contained a nearly saturated solution of the salt, containing 7·84 grammes metallic copper per 100 cubic centims., the formula $CuSO_4$ $36H_2O$ requiring 7·80) the value of R was found to be close to 110 ohms at the average temperature of the observations—this number being calculated from the dimensions of the column of fluid between the electrodes, and the specific resistance of the fluid determined by a new method which will be described in detail in a future paper. Similarly, the value of R for the zinc-sulphate voltameter was calculated to be close to 250 ohms.

The following numbers were obtained with copper-sulphate and copper electrodes :—

Surface of each electrode = 8·65 square centimetres.

(I.) *Values obtained when each electrode was new*, i. e. *polished compact rolled copper plate.*

Current, in microwebers.	Microwebers per square centimetre of electrode surface.	E, in volts.	CR.	$e=E-CR$.
7·1	0·8	·032	·001	·031
14·6	1·7	·033	·002	·031
23·8	2·7	·036	·003	·033
30·8	3·6	·036	·003	·033
35·7	4·1	·039	·004	·035
73·0	8·4	·047	·008	·039
148·0	17·1	·060	·016	·044
185·8	21·5	·062	·020	·042
247·0	28·6	·073	·027	·046
371·0	42·9	·088	·041	·047
728·0	84·2	·131	·080	·051

(II.) *Values obtained with electro-deposited copper on each electrode.*

(*a*) When the copper had been deposited some 48 hours, the electrodes being in the voltameter out of contact of air:—

15·2	1·7	·018	·002	·016
30·2	3·5	·025	·003	·022
91·5	10·6	·036	·010	·026
212·0	24·7	·050	·023	·027
403·0	46·6	·079	·044	·035
749·0	86·6	·137	·082	·055

(*b*) When the copper had not been deposited so long, from 15 to 20 hours after deposition :—

15·2	1·7	·015	·002	·013
22·8	2·6	·017	·003	·014
30·2	3·5	·020	·003	·017
45·0	5·2	·024	·005	·019
89·1	10·3	·033	·010	·023
253·0	29·2	·052	·028	·024
420·0	48·6	·078	·046	·032
774·0	89·6	·130	·085	·045
1328·0	153·5	·205	·146	·059

(*c*) When the copper had only been deposited a few minutes before each observation was made :—

16·6	1·9	·011	·002	·009
28·4	3·3	·014	·003	·011
42·3	4·9	·018	·005	·013
134·5	15·5	·031	·015	·016
240·0	27·7	·048	·026	·022
383·0	44·3	·070	·042	·026
740·0	85·5	·116	·081	·035
1311·0	151·6	·190	·144	·046

By interpolation, the following values for *e* are calculated from the above figures :—

Current, in microwebers.	I.	II*a*.	II*b*.	II*c*.
10	·031	—	—	—
20	·032	·017	·014	·010
50	·037	·023	·020	·013
100	·041	·026	·023	·015
200	·043	·027	·024	·020
500	·049	·043	·036	·029
1000	—	—	·050	·040

From which it is evident that the more freshly deposited the electro-copper was, the less was the value of e,—leading to the conclusion that either the freshly deposited copper had a higher power of "condensing" copper on its surface than rolled copper, thereby increasing the value of n_1 in the formula

$$e = \{h' + (1-n_1)H_1 + h''\}\chi J,$$

and that this power became lessened on standing, or else that, on standing, the surface of the copper altered in such a way as to cause the value of h'' to increase, or, possibly, that both changes took place together.

Precisely analogous results were obtained in other experiments with different voltameters: with considerably stronger currents up to some 5000 microwebers per square centimetre of electrode surface, values of 0·2 volt and upwards have been obtained for e by a method now being elaborated in conjunction with Mr. E. H. Rennie. Admitting that in these instances the values of h' and h'' are negligible compared with $(1-n_1)H_1$ (which probably is not quite the case), it results that the value of $H_1\chi J$ must exceed 0·2 volt, *i. e.* that H_1, the heat of transformation of "nascent" into ordinary copper, is greater than $\frac{0{\cdot}2 \times 10^8}{4410} = 4500$ gramme-degrees per gramme-equivalent.

94. In precisely the same way the following values were obtained on electrolysing a solution of zinc sulphate with bright zinc electrodes, the area of each of which was 8·6 square centims., the value of R being close to 250 ohms.

Current, in microwebers.	Microwebers per square centim. of electrode surface.	E, in volts.	CR.	e=E−CR.
14·3	1·7	·023	·004	·019
28·2	3·3	·031	·007	·024
39·4	4·6	·039	·010	·029
69·8	8·1	·050	·017	·033
87·9	10·2	·068	·022	·046
136·4	15·9	·085	·034	·051
167·1	19·4	·094	·042	·052
310·0	36·0	·131	·078	·053
647·0	75·2	·232	·162	·070
1147·0	132·5	·365	·287	·078

The curves traced out with zinc- and copper-sulphate solutions and zinc and copper poles respectively exhibit resemblance in general characters to those obtained with acidulated water and non-oxidizable electrodes: they indicate that e increases with the current but not so rapidly, so that the curves are concave downward.

95. Under certain conditions, the value of h'' in the formulæ arrived at in § 91, representing the counter E.M.F. set up during electrolysis, may become negative, but numerically greater than $h'+(1-n_1)H_1-n_1h_1$. In such a case negative work must be spent (or work will be gained) during the decomposition; the cell is then termed an electromotor, and constitutes an ordinary galvanic element. When this is the case, $E_3>E_1$,—as, for instance, when the + electrode is zinc and dilute sulphuric acid is electrolysed, or when copper sulphate is electrolysed as a partitioned cell, the one half containing zinc sulphate with a plate of zinc therein constituting the + electrode (Daniell's cell). The previous experiments show that the value of the expressions

$$h'+(1-n_1)H_1-n_1h_1 \quad \text{and} \quad h'+(1-n_1)H_1$$

(according as a gas or a solid is evolved at the negative electrode) are positive even with very small currents, and increase as the current increases. It hence results that the numerical value of the negative counter E.M.F. set up in a simple voltaic circuit of zinc, another metal, and dilute sulphuric acid, or in a Daniell's cell (*i. e.* the actual E.M.F. of the cell*), *must decrease as the current produced by it increases.*

* The E.M.F. of an electromotor is defined for the present purpose as *the difference of potential set up between two poles of the same material* (*e. g.* the two brass quadrants of an electrometer, or two copper conducting-wires, the one connected with one plate of the electromotor, the other with the other) *corrected for the effect of the current passing (if appreciable) due to the external resistance.* Whatever may be the influence of contact actions upon this corrected potential-difference in any given case, this influence must be constant for a given apparatus, and independent of the current generated, so that any change in the potential-difference set up is not due in any way to contact-action between the metallic plates and conducting-wires &c. The correction is of this form:—Let E_1 be the actual difference of potential and E_2 the E.M.F. of the electromotor, let R_1 be the external resistance and R_2 the resistance of the electromotor, and let C be the current passing (which $=0$ if R_1 is indefinitely great); then

In the case of a simple voltaic circuit, this effect is wholly distinct from one often observed in a newly set-up cell charged with dilute acid containing dissolved air. When first set to work the action of the cell is greatly intensified by the oxidation of the evolved hydrogen by the dissolved oxygen (much as is the case in a Leclanché element, the oxygen coming from the manganese dioxide); but by-and-by this ceases and the E.M.F. goes down. This effect is often said, vaguely and not strictly correctly, to be due to the plates becoming "polarized" by hydrogen, the which phrase really applies to the wholly different phenomenon now under consideration.

That the E.M.F. of a Daniell cell is somewhat less when generating a current than when no current passes has already been shown to be the case by Waltenhofen (*Sitzb. Akad. Wien*, xlix. 2, p. 229) and by Beetz, using a modification of the method of compensation (Pogg. *Ann.* cxlii. p. 581, 1871). Apparently, however, physicists generally are under the impression that the diminution in E.M.F., or "polarization" of the cell, thus produced is practically inappreciable: thus, for instance, within the last few months a determination of the value of v has been made in Sir W. Thomson's laboratory by R. Shida, by measuring the E.M.F. of a gravity Daniell, first, in electrostatic units (no current being generated), and then in electromagnetic units (a moderately powerful current being set up); the which method evidently can only be applied if the difference in the E.M.F. according as a current is generated or not is negligible (Brit. Assoc. Reports, 1880, p. 497). The same kind of remark applies to several other investigations published during the last few years.

96. *Decomposition of Dilute Sulphuric Acid with a Zinc Positive Electrode.*—On trying experiments with a zinc (amalgamated) positive electrode and a platinum electrode in the same way as those described in § 92, it was found that the numerical value of e was uniformly negative and decreased as the cur-

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$E_2=\frac{R_1+R_2}{R_1}$, $E_1=E_1+CR_2$. For the total work done by the current in a time t is $C^2(R_1+R_2)t$, which $=E_2Ct$, whilst the work done outside the electromotor is $C^2R_1t=E_1Ct$; whence

$$E_2=E_1\times\frac{R_1+R_2}{R_1}=E_1+R_2\times\frac{E_1}{R_1}=E_1+CR_2.$$

rent increased. So long as the current remained of a constant value the nature and dimensions of the external battery were immaterial; so that *the same value for* e *was obtained whether an external battery was actually applied, or whether the zinc-platinum couple was the sole electromotor in circuit*, provided that, by suitably adjusting the total resistance in circuit, the current was made the same. Thus the following average numbers were obtained with a cell containing dilute sulphuric acid of 10 grammes H_2SO_4 per 100 cubic centims., the plates each exposing 8·6 square centims. of surface, and being contained in a U-voltameter like those above described, of 1·1 square centim. bore, the centres of the plates being 13 centims. apart; so that, as the specific resistance of sulphuric acid of the strength used is close to 2·9 ohms at 18° (from Kohlrausch's numbers, *loc. cit. suprà*), the value of R was close to $\frac{13 \times 2{\cdot}9}{1{\cdot}1} = 34$ ohms :—

Current, in microwebers.	Microwebers per square centimetre.	E, in volts.	CR.	$-e = -(E - CR)$.
6·7	0·78	−·604	...	·604
9·8	1·14	−·589	...	·589
14·4	1·67	−·571	...	·571
23·2	2·7	−·547	·001	·548
41·0	4·8	−·519	·001	·520
58·5	6·8	−·493	·002	·495
96·0	11·2	−·442	·003	·445
135·6	15·8	−·395	·005	·400

Evidently the value of −(E−CR)—that is, the direct E.M.F. of the combination—decreases as the current increases, but not at the same rate, the diminution in the E.M.F. being less rapid than the increase in rate of flow.

97. *Daniell's Cell.*—In order to verify the deductions above made from the preceding experiments as to the variation of the E.M.F. of a Daniell's cell with the current produced, and so to amplify the observations of Waltenhofen and Beetz, the following experiments were made with two such cells arranged on the "gravity" principle—*i. e.* no porous cell being employed, but the copper plate being lowest and immersed in a saturated solution of copper sulphate, the zinc plate being uppermost and immersed in a solution of zinc sulphate of

lower specific gravity than the copper sulphate solution. In the first cell the active surface of each plate was about 15 square centims., and the resistance of the column of fluid between them was calculated, from the dimensions of the column and Kohlrausch's values for the specific resistances of copper and zinc sulphate solutions, to be about 4 ohms. In the second cell much smaller plates were used, exposing about 1 square centim. of active surface, the resistance of the column of fluid being calculated to be about 40 ohms.

First Cell.

Current, in microwebers.	Microwebers per square centimetre.	E, in volts.	CR.	$-e=-(E-CR)$.
0	0	−1·090	...	1·090
10·9	0·7	−1·090	...	1·090
36·3	2·4	−1·090	...	1·090
107·7	7·2	−1·077	...	1·077
267·2	17·8	−1·069	·001	1·070
530·5	35·4	−1·061	·002	1·063
1317·5	87·8	−1·054	·005	1·059

Second Cell.

Current, in microwebers.	Microwebers per square centimetre.	E, in volts.	CR.	$-e=-(E-CR)$.
0	0	−1·105	...	1·105
11·2	11	−1·105	...	1·105
36·8	37	−1·094	·001	1·095
109·1	109	−1·082	·004	1·086
265·5	266	−1·053	·010	1·063
515·5	516	−1·020	·021	1·041
1140·0	1140	−0·982	·046	1·028

In these experiments the correction CR is only approximate, it being impossible to calculate the precise value of R with any great degree of accuracy; but evidently, except in the last one or two determinations, even a large error in the value of R would make no appreciable difference in the end result, viz. *that the E.M.F. of a Daniell cell regularly decreases as the current produced increases, but not at so rapid a rate.*

During the time that these observations were being made, the changes in the E.M.F. of the cell due to "running down" and variation of the density of the solutions surrounding the two plates respectively, were too small to be capable of measurement. After making an observation with

a larger current and reducing the current to a smaller value or to *nil*, sensibly the same value was always obtained whether at the beginning or end of the series of measurements, which lasted some two or three hours in each case. If, however, observations were made one day and then repeated a day or two after, concordance was rarely noticeable between the results: the later experiments always showed a more rapid rate of fall in the numerical value of $-e$ with the current-increase than the earlier ones, and also generally indicated a perceptibly lower value when the current was *nil*. Apparently this result was due to the deposition of copper on the surface of the zinc plate, owing to diffusion.

Experiments are now in progress in which the true value of R for any given cell is determined by a new method: so far these have given results entirely confirming those above described. The highest values hitherto obtained for the E.M.F. of a freshly arranged Daniell's cell generating an indefinitely minute current only, and freed from complicating circumstances as far as possible (especially presence of dissolved air, which tends slightly to lower the value), are between 1·105 and 1·110 volt (Clark's cell being 1·457 volt) at the temperature of 15° or thereabouts. The discussion of these experiments and of the valuations of the E.M.F. of a Daniell cell made by previous observers, and of the bearing on the discrepancies between these valuations of the point just substantiated (viz. the dependence of the E.M.F. on the current generated) will be resumed in a future paper. It may be noticed, however, that even with a not very enormous rate of current-flow per unit area, the diminution in E.M.F. amounts to several per cent. of the highest value, a quantity quite sufficient to vitiate observations in which the E.M.F. is assumed to remain constant.

98. Similarly the E.M.F. of a Grove's cell is not wholly independent of the current generated, although the effect is somewhat less marked than with a Daniell cell. The end result of the chemical changes taking place in this cell are expressed by one or other of the equations

$$\mathrm{Zn} + \mathrm{H_2SO_4} + 2\mathrm{HNO_3} = \mathrm{ZnSO_4} + 2\mathrm{H_2O} + 2\mathrm{NO_2},$$
$$2\mathrm{Zn} + 2\mathrm{H_2SO_4} + 2\mathrm{HNO_3} = 2\mathrm{ZnSO_4} + 3\mathrm{H_2O} + \mathrm{N_2O_3},$$
$$3\mathrm{Zn} + 3\mathrm{H_2SO_4} + 2\mathrm{HNO_3} = 3\mathrm{ZnSO_4} + 4\mathrm{H_2O} + 2\mathrm{NO};$$

so that, in addition to the production of gases (more or less completely absorbed by the nitric acid), dilution of the nitric acid takes places in the proximity of the platinum plate, thereby causing h' (the correction for the effects of differences in the density of the fluids surrounding the electrodes) to have an appreciable value. It is therefore to be expected that the E.M.F. of a Grove's cell will, like that of a Daniell's or an ordinary voltaic circle, decrease with the current generated. That this is actually the case is indicated by the following figures obtained with a "gravity" Grove's cell, the plates of which exposed an actual surface of 8 square centims. each, the calculated resistance of the column of fluid (partly concentrated nitric acid, partly 5-per-cent. sulphuric acid solution) between the plates being about 2 ohms, and the zinc plate being well amalgamated.

Current, in microwebers.	Microwebers per square centimetre.	E, in volts.	CR.	$-e=-(E-CR)$.
0	0	−1·872	...	1·872
9·4	1·2	−1·872	...	1·872
18·7	2·3	−1·872	...	1·872
36·4	4·6	−1·872	...	1·872
93·6	11·7	−1·872	...	1·872
187·2	23·4	−1·872	...	1·872
466·2	58·3	−1·867	·001	1·768
930·5	116·3	−1·861	·002	1·863
1850·0	231·3	−1·850	·004	1·854
3678·0	459·8	−1·839	·007	1·846
8955·0	1119·4	−1·791	·018	1·809
17480·0	2185·0	−1·747	·035	1·782

99. It hence results that all methods for determining the E.M.F. of voltaic combinations, or for determining the internal resistance of cells, which depend on the production of currents of different magnitudes by means of the voltaic combination employed, may be erroneous to a considerable extent when it is assumed (as is ordinarily done) that the E.M.F. of the combination is independent of the current generated, and when the voltaic combination is such that this assumption is untrue, which is the case apparently in all the more common forms of cells, if indeed it is not universally the case. Thus, for instance, in Ohm's method for determining the E.M.F. of a cell, the current C_1 produced by the cell when connected with a galvanometer, the total resistance in circuit being R_1, is determined;

an additional resistance R_2 is then introduced, and the new current C_2 again determined. If the galvanometer be a sine-galvanometer, and α and β are the deflections in the two cases respectively,

$$C_1 = K \sin \alpha \text{ and } C_2 = K \sin \beta,$$

where K is a constant for the instrument. If the E.M.F. of the cell be supposed to be the same (E) for both currents, then

$$C_1 = K \sin \alpha = \frac{E}{R_1},$$

and

$$C_2 = K \sin \beta = \frac{E}{R_1 + R_2};$$

whence

$$E = K \,.\, R_2 \frac{\sin \alpha \,.\, \sin \beta}{\sin \alpha - \sin \beta}$$

$$= C_1 R_2 \frac{\sin \beta}{\sin \alpha - \sin \beta}$$

$$= C_2 R_2 \frac{\sin \alpha}{\sin \alpha - \sin \beta};$$

that is, E is known in terms of the currents, the deflections, and the added resistance R_2.

But if E be not the same for the two currents, being greater for the smaller by an amount δE, the equations become

$$C_1 = K \sin \alpha = \frac{E}{R_1},$$

and

$$C_2 = K \sin \beta = \frac{E + \delta E}{R_1 + R_2} = \frac{(1+\delta)E}{R_1 + R_2};$$

whence

$$(1+\delta)E = K \,.\, \sin \alpha \,.\, R_2 \frac{\sin \beta}{\sin \alpha - \frac{\sin \beta}{1+\delta}}.$$

Evidently, if δ be assumed $=0$, the value of this expression is greater than the value when δ is not $= 0$; that is, the assumption that the E.M.F. of the cell is constant throughout leads to the calculation of a value for its E.M.F. greater than the true value for the smaller current, and *à fortiori* greater than the true value for the larger current*.

* In H. F. Weber's experiments on the value of J (§ 55), a trifling source of error exists in those observations made with a voltaic battery,

In just the same way an incorrect value is obtained for the internal resistance of a cell by Ohm's method, which depends on the same principles. If R_1 be the resistance of the cell and R that of the rest of the circuit, a current is generated

$$C_1 = K \sin \alpha = \frac{E}{R + R_1},$$

and by throwing in an extra resistance R_2 the current is reduced to

$$C_2 = K \sin \beta = \frac{E(1+\delta)}{R + R_1 + R}.$$

If it be assumed that $\delta = 0$, then

$$R_1 = R_2 \frac{\sin \beta}{\sin \alpha - \sin \beta} - R;$$

but if δ is not equal to 0, then

$$R_1 = R_2 \frac{\sin \beta}{(1+\delta) \sin \alpha - \sin \beta} - R,$$

which is manifestly less than the former value; so that the assumption that the E.M.F. of the cell is constant throughout leads to the overvaluation of its internal resistance.

100. The results above described have an important bearing on a considerable amount of work performed by Favre (*Comptes Rendus*, 1866 and following years). By passing a current through an electrolytic cell placed in a calorimeter, an external resistance being in circuit so large that the resistance of the cell was wholly negligible (?) in comparison with it, and consequently the heat developed in accordance with Joule's law was practically *nil*, Favre obtained values in terms of heat corresponding to the difference between the work done in decomposing the electrolyte into the primary and the final products of decomposition. *E. g.* in one set of experiments with water, the actual mean heat-development was close to 14,000 gramme-degrees per gramme-

---

the mean E.M.F. of which during the experiment was measured as a necessary part of the data; for the measurement gives the E.M.F. corresponding to a current C_1, whilst the heat evolved was that caused by a different current C_2. As, however, Weber states that C_1 was always approximately $= C_2$, this source of error is not great and is probably negligible, since the B.A. resistance values got by this method are sensibly the same as those obtained by the two other independent methods employed.

equivalent of water decomposed; adding to this 34,100 gramme-degrees, the heat corresponding to the formation of gaseous oxygen and hydrogen (Part I. § 31), it results that in this experiment the total work done during the electrolysis was equivalent to 48,100 gramme-degrees, or 2·12 volts; *i. e.* the mean value of *e* in these experiments was 2·12 volts. By comparing together various values obtained in this way with different electrolytes, Favre was led to the conclusion that of this 14,000 gramme-degrees (which he regarded as a constant heat-absorption during water-electrolysis over and above the heat taken up in the formation of gaseous oxygen and hydrogen =34,100), about 9500 were due to the transformation of allotropic oxygen formed by the first action of the current into ordinary oxygen gas, and the remainder to the transformation of allotropic hydrogen into ordinary hydrogen gas. The above-described results, however, indicate that these particular numerical values have only reference to the particular apparatus and current-strengths used by Favre: had the size of the electrodes been varied, or their nature, or the current-strength, quite different numbers would have been obtained in each case, not only in these particular experiments cited, but also in a number of other analogous ones with other substances; for each change would have brought about a corresponding change in the value of *e*, and hence in the heat-evolution. Apart from this, however, as Favre's values were obtained with the mercury-calorimeter, a considerable probable error attends the determinations; so that finally no reliance at all can be placed on the conclusions arrived at by Favre in this series of experiments, as regards numerical values.

It is noticeable in this connexion, that experiments by Raoult (*Annales de Chimie et de Phys.* ii. p. 317, and iv. p. 392, 1864 and 1865) show that the value of the counter electromotive force set up during electrolysis varies with the current *cæteris paribus*. Raoult observed the "subsequent polarization" of an electrolytic cell very quickly after the rupture of the current, determining it in terms of a Daniell's cell, this being itself valued in terms of the heat producible by its current whilst a gramme-equivalent of copper was precipitated. The difference between the heat actually evolved in

the cell (measured by a calorimeter) and that equivalent to the polarization, was termed by Raoult "Local Heat," and found by him to be larger with stronger currents. The results above described with a Daniell cell, however, show that the valuation in terms of heat of a Daniell cell is not a constant quantity; for the heat capable of being evolved by the current outside the battery during the precipitation of a gramme-equivalent of copper, being proportional to the E.M.F. of the cell, is variable with the time during which this precipitation takes place, *i. e.* with the strength of the current; whilst the "subsequent polarization," measured by Raoult, being always more or less inferior to the counter E.M.F. set up during the passage of the current, is not the true measure of the electrolytic work done by the current whilst it was passing through the cell.

Notwithstanding, however, that the numerical results of Favre and Raoult are open to exception, these observers were amongst the first, if not actually the first, to attempt to carry out experimentally some of the lines of research opened out by Sir W. Thomson (1851 paper), although the theoretical aspects of the question, as discussed by them, do not entirely coincide with Thomson's mode of reasoning.

Summary of Results.

101. The following summary briefly indicates the salient results arrived at in Parts III. and IV. of these researches.

(1) The passage of a given quantity of electricity through an electrolyte causes the decomposition of one and the same amount of substance, irrespective of the time taken in its passage; in other words, conduction without electrolysis does not take place, and Faraday's law is true for excessively minute currents as well as for those of considerable magnitude.

(2) With very feeble currents, however, and with certain electrolytes, *e. g.* water, the quantity of products of decomposition actually collected after a given time, does not absolutely correspond to the quantity of electricity that has passed, even after various sources of suppression have been eliminated, such as occlusion in or condensation on the electrodes, solution in the fluid, or suppression by the chemical action of dissolved gases. The cause of this is the "diffusion discharge"

produced (in the case of water) by the diffusion towards the − electrode of water containing dissolved oxygen, and towards the + electrode of fluid containing dissolved hydrogen (and similarly in other cases), thus causing an unavoidable suppression by chemical action. When the amount of suppression due to this cause is determined and added to the observed amount of decomposition, the total corresponds exactly with the quantity of electricity that has passed.

(3) In the electrolysis of acidulated water, until the sources of loss of hydrogen other than "diffusion discharge" are eliminated (viz. solution in the fluid, condensation and absorption by the electrode, and action of dissolved oxygen originally present in the fluid), the counter E.M.F. set up when a given steady current traverses a given voltameter is short of its maximum value for that current; simultaneously a deficiency in the amount of hydrogen collected as compared with that due to the quantity of electricity passing is noticed (even after correction for diffusion discharge); whilst on breaking circuit, the rate of fall of the "polarization" of the electrodes is more rapid than its minimum value for that current. On the other hand, as soon as the counter E.M.F. reaches its maximum, the deficiency in hydrogen disappears (after correction for diffusion discharge), and the rate of fall of the polarization after breaking circuit reaches its minimum. The more nearly completely the sources of loss are eliminated, the more nearly does the counter E.M.F. set up approach its maximum, the less is the deficiency in the hydrogen collected, and the more nearly does the rate in fall of polarization approach its minimum.

(4) A theory has been enunciated, and more or less completely demonstrated, which reconciles the hitherto apparently contradictory numerical values obtained by previous observers for the counter E.M.F. set up during electrolysis, the "subsequent polarization" existing after rupture of the current, and the E.M.F. of gas batteries. In accordance with this theory, the relationships between the current flowing and the counter E.M.F. set up in an electrolytic cell are expressed by the following formula :—

$$e = \mathrm{E} + [\Sigma\{(1-n)\mathrm{H}\} - \Sigma(nh) - \Sigma(\mathbf{H})]\chi\mathrm{J}.$$

(5) In the case of all the electrolytes examined, the value

of e is found to increase as the current increases, but at a less rapid rate, so that the curves traced out by plotting currents as abscissæ and counter E.M.F. values as ordinates are concave downwards.

So long as the rate of flow per unit area of electrode surface remains the same, the value of e is constant; *i. e.* if the electrode surface and the current vary in the same way, then e remains the same. With a given current increasing the electrode surface diminishes the value of e.

The values of e depend on the material of which the electrodes are made. Other things being equal, carbon gives higher values than platinum, and platinum than gold.

In the case of acidulated water, rendering the solution more dilute increases the value of e.

From former observers' work it results that increasing the temperature decreases e.

(6) The above formula, in conjunction with experimental determinations of the variations in the values of e under various conditions, explains coherently and quantitatively the leading facts connected with counter E.M.F., polarization, and the E.M.F. of gas-batteries, and accounts for the possibility, under certain conditions, of decomposing an electrolyte with a less battery E.M.F. than corresponds to the work done in splitting it up into the final products—and also indicates that the E.M.F. of a Daniell cell is not constant, but is less the greater the current it generates, to such an extent that with currents of not very great magnitude a diminution in E.M.F. to the extent of several per cent. is brought about, and that, in consequence, certain of the methods in use for determining the E.M.F. of cells and their internal resistance are, at any rate for certain kinds of cells, incorrect, as they are based on the assumption that the E.M.F. of the cell is constant.

(7) By means of the above formula and the experimental determinations of the causes which make e to vary, &c., information can be deduced as to the amount of energy with which gases are condensed upon the surface of solids, and in particular as to the amount of energy requisite to break up an electrolyte into "nascent" products solely. By conjoining this determination with the determination of the methods for finding the E.M.F. corresponding to the energy requisite to

break it up into the final products (described in Parts I. and II.), information can be deduced concerning the affinity of the constituents of the electrolyte, and the variations of that affinity according as the constituents are "nascent" or in their ordinary free state. For instance, the energy given out in the transformation of nascent hydrogen and oxygen into the ordinary free gases exceeds the energy that would be developed by the union of these gases to form liquid water, *i. e.* exceeds the energy equivalent to 34100 gramme-degrees or to 1·50 volt.

PROCEEDINGS
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MAY 1881.

XVII. *On the Rate of the Decrease of the Light given off by a Phosphorescent Surface.* *By* Lieut. L. DARWIN, R.E.*

I CARRIED out a series of experiments at Chatham with the view of determining the law of the rate of decrease of the light of a phosphorescent surface. The experiments were conducted by comparing the light given off by a surface covered with Balmain's luminous paint, with a sheet of tissue paper illuminated from the further side by a Sugg's burner regulated to give about the light of four standard candles. The surface coated with paint was one side of a thin metal vessel, which was filled with a mixture of ice and water; the object of this was to keep the temperature as uniform as possible, as any increase of temperature increases the light given off by the paint. A sheet of tissue paper, of about the same size as the painted surface, was arranged just above it so that the light of the burner illuminated the tissue paper from the further side to the observer. The whole was enclosed in a box with an opening at one side, through which the light of the burner reached the tissue paper only, and opposite to it a small hole through which the observations were made. In this way only the light from the two surfaces reached the eye, and the light of the room did not reach the

* Read December 16, 1880.

surface of paint. Besides these reasons for observing through a small hole, it is better to do so, because the light given off by the illuminated tissue seems to vary with the angle at which it is observed, and the readings would not be constant if the eye were not in a fixed position. Experiment showed that the diffused light in the box from the illuminated tissue paper was not enough to have any effect on the phosphorescent paint. Both the paint and the tissue were observed through a solution of cupric sulphate, and blue glass; this did not, as far as I could see, cause any alteration in the colour of the paint. If the blue glass alone was used, the tissue looked pink in comparison with the paint; and with the cupric sulphate solution alone it looked green; but with the two the colour was so nearly imitated, that when the intensity of the light was the same I could only distinguish the two surfaces by their positions.

The illumination of the tissue was estimated by the distance of the burner from the tissue; this assumes that the light given off by the tissue varies directly as the light striking it on the reverse side. Bright sunlight was reflected onto the painted surface by a mirror; and after it had acted for a few seconds, the room was darkened, with the exception of the light of the standard burner. For five minutes before this time, I took the precaution of hiding my eyes, so that no light could get at them. As soon after this as possible, observations were taken. Two slightly different methods were employed. At first the burner was placed at a definite distance from the tissue, and the time was noted at which the paint and tissue first appeared to be equally bright, and also that at which they first appeared to differ again in illumination; the mean of these two times was taken as the time of equal illumination. The burner was then moved away to a further fixed position, and another observation taken in the same manner. After five observations had been taken in this way, the rate of decrease of the light became very slow, and this method did not work well. The distance of the burner to obtain equal illumination was then found by moving it backwards and forwards, and noting the position at which the illumination of the two surfaces appeared the same; this was done four times as rapidly as possible, two before and two after the time at which an

observation was wanted. The following table gives the mean of two series taken in this manner. The first column gives the illumination of the paint: the light given off by the tissue when the burner was nine inches from it is taken arbitrarily as 100; and the other illuminations are calculated accordingly from the distance of the burner. No absolute standard was attempted, as the light of the tissue would vary with its thickness, probably with the angle at which it was observed, and with the exactness with which the colour of the paint was imitated by means of the glass and solution. The second column gives the time at which the observation was taken.

TABLE.

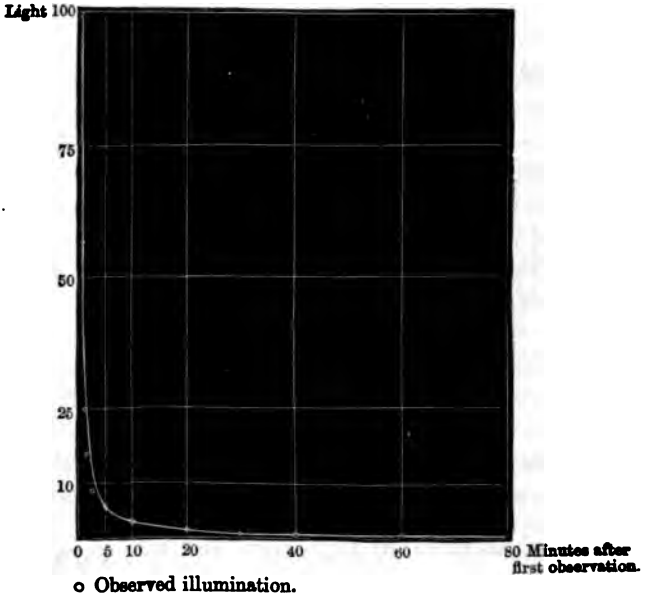
Observed Light.	Observed Time.	Calculated Time.
	m. s.	m. s.
100·	0 0	0 0*
56·5	18	19
25·1	45	1 8
14·1	1 33	2 11
9·04	2 34	3 25
6·10	5 0	5 0*
2·89	10 0	9 59
1·34	20 0	19 53
·782	30 0	31 52
·604	40 0	39 41
·433	50 0	53 0
·376	60 0	60 0*
·285	80 0	76 14

I also made an attempt to calculate a curve which should as nearly as possible coincide with these results. The form of the curve which naturally suggested itself was $\frac{A}{t+B}=l^c$; t=time, l=light, A, B, and C being constants. A curve of this form to pass through three points (*) was calculated: A=26·1, B=·498 minute, C=·86. That is to say, the rate of decrease of the light varies as the light to the power of 1·86; and at that rate the light would have been infinitely great 30 seconds before the first observation. Taking the illuminations as obtained from the observations, the time of the observations was calculated according to the above formula; and the result is given in the third column. Three of the observed times differ from the calculated times

more than can be accounted for by errors of observation; and it appears that the equation does not give quite the correct curve. From this and from another series of observations, it appears that in its lower parts the curve is very nearly of the form $\frac{A}{t+B}=l$; that is to say, that the rate of decrease of the light varies as the square of the light.

By comparing several series of observations it appears to me that the rate of decrease is quite independent of the intensity of the first illumination.

Diagram showing the Rate of Decrease of the Light given off by Phosphorescent Paint.



o Observed illumination.

—— Curve calculated from the equation $y^{\cdot 26}=\frac{26\cdot1}{x+\cdot496}$.

XVIII. *Notes on the Construction of the Photophone.*

By Professor Silvanus P. Thompson*.

(1) In the selenium photophone, light of varying intensity is received upon a prepared surface of sensitive crystalline selenium, the electric resistance of which it thereby changes.

* Read January 22, 1881.

In the construction of the receiving "cell" it is obvious that certain relations must hold between the dimensions of the sensitive surface and the degree in which a given quantity of light will change the electric resistance—relations which ought to be observed in the construction of the instrument, and which are certainly worthy of investigation.

Professor Bell's typical selenium-cell consists of a small cylinder about 2 inches in diameter and 2½ inches in length (giving at most a superficial area of 15·8 square inches available), built up of alternate disks of brass and mica, filled between the edges of the brass disks with selenium, and having alternate brass disks connected up in multiple arc. This cell, in his usual apparatus, is placed at the bottom of a parabolic mirror.

Certain experimental observations made in attempting to repeat Prof. Bell's experiments led the writer to query whether this arrangement was the best possible one, and suggested an investigation, of which the following paragraphs are the chief points.

(2) THEOREM I.—*With a given maximum of incident light distributed uniformly over the surface, the change of electric resistance in a selenium-cell will vary proportionally with its linear dimensions, provided its parts be arranged so that on whatever scale constructed the normal resistance shall remain the same.*

Suppose there to be a cell of a certain size, having a certain normal resistance (*i. e.* a certain resistance in the dark as measured under a standard electromotive force), and presenting a certain area of surface; then, if a perfectly similar cell be made on a scale n times as great (in linear measure each way), the same total amount of light falling upon its surface will produce n times as great a variation in the electric resistance.

The proof of this theorem depends upon the law discovered by Professor W. G. Adams *—namely, that *the change in the resistance of selenium is directly as the square root of the illuminating-power.*

For let it be supposed (as in the proviso of the theorem, introduced so as not to complicate the electrical conditions) that the enlargement should be to the scale $n:1$ in all respects, save only in the depth of the selenium film, the brass con-

* Proc. Roy. Soc. vol. xxv. 1876, p. 113.

ductors being the same in number as before, but of n times their former size, touching selenium along edges n times as long as before, the intervening selenium films being n times as broad as before. Such an enlargement will leave the normal electric resistance where it was before, provided the depth of the selenium films be not increased—though, as the photo-electric action is almost entirely a surface action, a slight increase in the depth of the film would probably produce no great change in its electric sensitiveness.

Suppose the light to be caused, by appropriate optic means, to fall upon the whole enlarged surface uniformly. The linear dimensions being increased in the ratio $n : 1$, the area will be increased as $n^2 : 1$. The average intensity of the illumination will now be $\frac{1}{n^2}$ of what it was. Each portion of surface equal to the original surface will receive but $\frac{1}{n^2}$ part of the whole light.

But by Adams's law the change of electric resistance is proportional to the square root of the illumination. Hence the electric effect over each portion of surface equal to the original surface will be $\frac{1}{n}$ of the original electric effect; and, since the effect is proportional also to the amount of surface which is under illumination, this quantity $\frac{1}{n}$ multiplied into the ratio of the enlarged surface to the former surface ($n^2 : 1$), gives for the total electric sensitiveness of the enlarged cell a value n times as great as that of the original cell. Thus the proposition is proved.

(3) THEOREM II.—*With a given maximum of incident light the change of electric resistance will vary in proportion to the third power of the linear dimensions of the cell, if, while its linear dimensions are increased, the absolute thicknesses of the brass conductors and of the selenium films remain the same as before, and their number be proportionately increased.*

It was supposed above that the surface was increased n times by an enlargement in length and breadth, which left the total normal resistance where it was before. But since the breadth of the films is dictated solely by practical considerations of construction, the increase of linear width to n times will en-

able n times as many conductors to be employed; and the thickness of the selenium film may be reduced to $\frac{1}{n}$ of what it was reckoned above. This will reduce the total normal resistance of the cell to $\frac{1}{n^2}$ of what it was reckoned above, and would therefore make it n^2 times as sensitive were its resistance the only one in the circuit.

Combining this result with the former, we obtain the result that the change of electric resistance exhibited by the cell of linear dimensions n, under the influence of a given quantity of light distributed uniformly over its surface, will be n^3 times as great as that exhibited by a cell of linear dimensions 1, provided that the absolute thickness of the films and conductors remain the same (the resistance of the brass conductors themselves being reckoned small).

(4) The practical inference from this is, that the selenium-cells should be made as large as possible, and that the beam of light received by the mirror from the distant station should be so constructed as not to concentrate the light on one point of the selenium, but to distribute it uniformly over the sensitive surface.

Now the supposed advantage of the parabolic mirrors hitherto employed is that they collect parallel rays to one focus. If this be no longer necessary or advisable, then some other form of mirror than that of the paraboloid of revolution ought to be employed.

(5) A short cone, polished on the interior surface, appears therefore to offer certain advantages over the paraboloid in respect of its distribution of light, besides being far cheaper to construct. It only remains to calculate the appropriate angle of aperture that shall, with a cylindrical selenium-cell of given length, give the greatest available linear aperture and reflect into the cell the greatest number of effective rays.

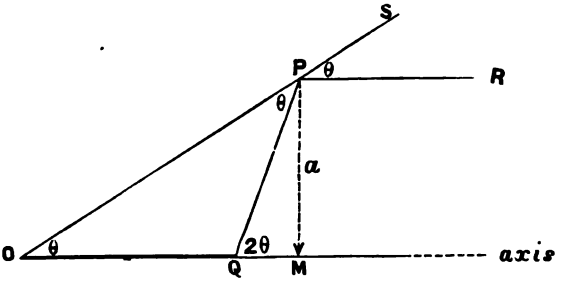
(6) THEOREM III. *A hollow cone along whose axis lies a cylindrical selenium-cell of given length will reflect onto that cylindrical surface the greatest number of rays* (that traverse space parallel to the axis) *if its angular semi-aperture be* 45°.

The calculation amounts to finding the angle that will, with

a given length of cell, give the greatest possible linear aperture.

In the figure 1, let POM represent the angle of half-aperture, which we will call θ. Let O Q ($=l$) be the length of cylinder, which may be supposed to be thin. Let the ray R P, P Q, be drawn making equal angles of incidence and reflexion with the surface of the cone. Then, since P R is parallel to the axis of the cone, the angle S P R=Q P O=θ, and the triangle O Q P is isosceles. Hence the exterior angle P Q M=2θ. If P M be drawn from P perpendicular to the axis, its length, which we may call a, will be that of the half-aperture.

Fig. 1.



Now $$\sin \mathrm{P\,Q\,M} = \sin 2\theta = \frac{a}{\mathrm{P\,Q}};$$

therefore $$a = \mathrm{P\,Q} \sin 2\theta,$$

$$a = l \sin 2\theta.$$

Hence if l be constant, a will be a maximum when $\frac{da}{d\theta} = 0$.

Now $\frac{da}{d\theta} = l \cos 2\theta$; and equating to zero we find

$$\cos 2\theta = 0,$$

$$2\theta = 90°,$$

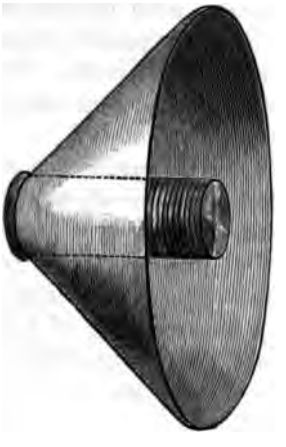
or $$\theta = 45°.$$

In other words, the mirror cone must have an apparent vertical angle of 90°, and its development will be a sector of 254° 33′·6 $\left(=\frac{360°}{\sqrt{2}}\right)$ cut from a circle whose radius is $\sqrt{2} \times$ O Q.

If the cylinder cell have itself a radius r, then the whole diameter of the linear aperture will be equal to 2 $(l+r)$; and the cone may be conveniently truncated at a distance along the axis from O equal to r, which would leave a circle of $2r$ diameter just fitting the posterior end of the cylinder.

It may be remarked that the anterior end of the cylinder will, when it is placed in position, be in the same plane as the circular mouth of the mirror cone, and the general appearance of the mirror and cylinder will be that presented in figure 2.

Fig. 2.



With an angular aperture less than 90°, the depth of the mirror from back to front must be greater than the length of the cylinder ; and the mirror, however prolonged, could not bring more rays to the surface of the cylinder except they underwent more than one reflexion.

If the angular aperture should be greater than 90°, the diameter of the cone that will reflect the effective rays will be less than that of the 90° cone, and hence cannot gather as much light.

One advantage possessed by such a mirror cone of the form specified above over any other form, parabolic or otherwise, is that all the rays meet the sensitive surface of the cylinder at normal incidence, and the loss by reflexion will be therefore a minimum.

(7) In preparing to repeat the Photophone experiments, the author has constructed sundry cells in a manner somewhat differing from that adopted by Professor Bell.

Finding it laborious to cut and fix the alternate disks of mica and brass, he constructed a cell by winding brass wires spirally round a glass tube so that the successive convolutions did not quite touch. Selenium was afterwards applied in the interstices, and alternate convolutions were connected

metallically, the wires being cut and then soldered with alternate junctions. Afterwards two parallel wires, wound side by side as in a double-threaded screw, were employed. One of these cells was found by the author on Oct. 19th to have as small a resistance (in the dark) as 240 ohms. On account, however, of the wire not adhering firmly to the glass, and from other causes, the arrangement, though far more easily constructed than the built-up cell, was not satisfactory. Taking a hint from Mr. Shelford Bidwell, who has recently published a communication on the Photophone in 'Nature,' the author has constructed cylinders of slate grooved with a fine double-threaded screw, in which the parallel wires are laid. These cells prove much more satisfactory. Experiments are now proceeding with cells of this kind varying in length from two to eight inches.

(8) The theorems enunciated above concerning the advantages of enlarging the size of the selenium-cell can readily be put to experimental test with cells such as described. There is of course a practical limit beyond which further increase of size will be of no advantage—such a limit being determined in particular cases by the resistance of the telephones and of the telephone-circuit, and by the other conditions, electrical and optical, of the experiment.

University College, Bristol,
Nov. 24, 1880.

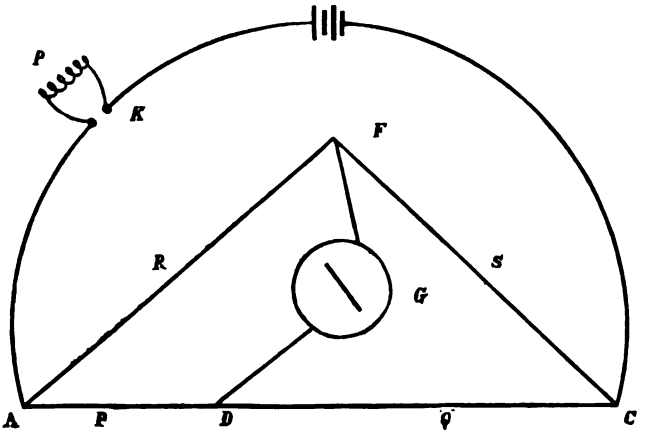
XIX. *On the Measurement of Small Resistances.* *By* R. T. Glazebrook, *M.A., Fellow of Trinity College, and Demonstrator of Experimental Physics at the Cavendish Laboratory, Cambridge**.

While measuring some small resistances with a Wheatstone's bridge at the Cavendish Laboratory, Mr. W. B. Allcock observed that the apparent measure of the resistance varied with the resistance in the battery circuit.

Let A D C be the bridge-wire, D being the point at which the sliding contact is to be made. Let P be the resistance of A D, Q that of D C (P and Q include the resistances added

* Read January 22, 1881.

to the ends of the bridge-wire), A F the resistance R to be measured, F C the standard S with which R is to be compared. At K in the battery circuit is a key.



In one position of the key the battery-current has to pass through the resistance ρ; in the other the ends of the coil ρ are connected, and it is thrown out of the circuit.

The experiment is as follows:—Place the key so that the resistance ρ is shunted, and adjust the position of D until there is no current through the galvanometer. Raise the key, and so throw ρ into the battery circuit; then the galvanometer-needle is considerably deflected, if the other resistances be small compared with ρ.

The experiment may of course be conducted in the reverse way, the position of equilibrium being found when ρ is in circuit. On depressing the key and shunting ρ the needle is deflected.

The deflection in this case is much greater than in the former; but then the battery-current is increased many times by the operation, and the apparatus therefore is rendered more sensitive; so that part of the effect may be due to a slight error in the original position of D.

The effect was reversed by changing the direction of the battery-current. This last fact showed that it could not spring from any heating of the coils. Moreover any heating-effect would be due to the difference in the temperature-coefficients of

R and S or P and Q respectively; but R and S were throughout as nearly as possible equal and similar, as also were P and Q.

But it is well known that a thermoelectric effect is produced by the contact at D. This, as will shortly be shown, will explain the phenomenon; and the effect may be made a means of measuring, approximately at least, the electromotive force set up at the junction. For let E be the E.M.F. of the battery, e that at the junction; then we may show that the current through the galvanometer is

$$x=\frac{E(QR-SP)+e\{B(Q+R+S+P)+(P+Q)(S+R)\}}{D} \quad (1)$$

B being the resistance in the battery circuit, and D a function of the resistances with which we are not at present concerned.

The condition for no current, therefore, is

$$0=E(QR-SP)+e\{B(Q+R+S+P)+(P+Q)(S+R)\},$$

and in the case in which the resistances to be measured are very nearly equal we may put P=Q, R=S, in the coefficient of e, so that

$$\frac{P}{Q}=\frac{R}{S}+\frac{e}{E}\left\{2B\left(\frac{1}{R}+\frac{1}{P}\right)+4\right\}. \quad (2)$$

Thus if B is large compared with R and P, the term involving e is appreciable, and the usual condition P : Q = R : S is not sufficiently nearly true to give correct results.

The equation shows that the sign of the correction changes with that of E.

Let P′ and Q′ be the values of P and Q when the battery resistance is large.

Then

$$\frac{P'}{Q'}=\frac{P}{Q}+\frac{e}{E}\left\{2B\left(\frac{1}{R}+\frac{1}{P}\right)+4\right\},$$

and

$$e=\frac{E\left(\frac{P'}{Q'}-\frac{P}{Q}\right)}{2B\left(\frac{1}{R}+\frac{1}{P}\right)+4}. \quad (3)$$

With the view of testing the truth of this explanation, I

made a series of experiments, using a wire bridge and various small resistances.

The resistance of the bridge-wire in the experiments was ·08 ohm; the wire was a metre long, and graduated to millimetres.

Different observations for the value of P agree to a fraction of a millimetre of the bridge-wire, while the differences in the values of P′ never amounted to more than 4 millimetres, and were usually much less. The value of ρ was 150 ohms. In some of the experiments Leclanché cells were used, in others Daniells. The E.M.F. of the Leclanché cells was found by the potentiometer method to be about 1·25 Daniell.

In the results given in the table, the E.M.F. of a Daniell cell is taken as 1 volt. The battery resistance is neglected compared with the 150 ohms interposed.

Table giving Results of Experiments.

No. of cells.	Bridge-reading for P.	Bridge-reading for P′.	R in ohms.	Resistance added to arms of bridge.	e in volts.
	mm.	mm.			
3 Leclanchés ...	501·2	504·9	2·02	0	$75{\cdot}10^{-7}$
2 do., multiple arc	501·2	510·2	2·02	0	$60{\cdot}10^{-7}$
1 Leclanché.....	496·1	472·9	·04	0	$75{\cdot}10^{-7}$
1 Leclanché.....	544·6	526·3	2·02	2·2	$65{\cdot}10^{-7}$
1 Leclanché.....	705·5	644·0	2·02	5·2	$63{\cdot}10^{-7}$
1 Daniell	500·8	467·5	·02	0	$60{\cdot}10^{-7}$
1 Daniell	507·5	489·0	·04	0	$63{\cdot}10^{-7}$

Thus the mean value of e as given by the experiments with the Leclanché cells is $77{\cdot}6 \times 10^{-7}$ volt, while that as given by the Daniells is $61{\cdot}5 \times 10^{-7}$ volt. The wire of the bridge and the contact piece are platinum-iridium, the other wires are copper.

The closeness in the values of e would appear to show that the assumption of some action at this junction will account for most of the phenomena; while the constancy of the effect shows that, if due to a difference of temperature between the bridge-wire and the contact piece, that difference cannot vary much.

The hand of the experimenter was separated from the metal of the contact piece by a cap of wood. The effect of maintaining contact for some time after finding the equilibrium-position was tried without result. If the junctions A and C of the platinum-wire and the battery circuit be heated, the effect is decreased; if they be cooled, it is increased. Thus the effect, if thermoelectric, is due to heating at D.

In making measurements of resistance, this effect can of course be eliminated in various ways; it appears, however, to be worth while to call attention to its existence. One method frequently adopted to correct for this thermo-electric effect is given by Prof. Chrystal and Mr. Saunders (Report on the Standard Units of Resistance, B.A. Report 1876, p. 13). They made contact with the sliding piece before making the battery-contact, and waited until the thermo-electric current had attained a steady value and the galvanometer-needle come to rest in a position slightly disturbed from its original one. If on making the battery-contact no effect was produced, the resistance is given by the ordinary equation $P : Q = R : S$. This of course is only applicable when none of the coils used have any appreciable self-induction.

Another method is to reverse the battery-current.

Let P_1 Q_1 be the values of P Q when the current is in one direction, P_2 Q_2 when it is in the other. Then the true value of $\frac{R}{S}$ is

$$\tfrac{1}{2}\left(\frac{P_1}{Q_1}+\frac{P_2}{Q_2}\right).$$

A third method, applicable to coils with no self-induction, is to interchange the battery and the galvanometer. The thermo-electromotive force is then superposed on that of the battery, and the condition $PS = QR$ holds. The most serious objection to this seems to be that the whole current must pass through the sliding junction, which may thus get considerably heated, and so damage the bridge-wire. Perhaps the simplest correction is to keep the battery resistance low compared with the others.

I tried the effect of using copper wire for the bridge in order to have only one metal throughout; but I found that the contact between my fingers of two pieces of copper wire

of somewhat different thickness produced a very appreciable current.

In the experiments given above the E.M.F. produced is about equal to that of a copper and platinum couple in which the difference of temperature is between 2° and 3°.

I was assisted in making the experiments by Mr. E. B. Sargant, Scholar of Trinity College.

XX. *Determination of the Density of Fluid Bismuth by means of the Oncosimeter.* *By* Professor W. Chandler Roberts, *F.R.S., and* Thomas Wrightson, *Memb. Inst. C.E.**

Some time since, one of us described the results of experiments made to determine the density of metallic silver and of certain alloys of silver and copper when in a molten state†. The method adopted was that devised by Mr. R. Mallet‡; and the details were as follows:—A conical vessel of best thin Low-Moor plate (1 millim. thick), about 16 centims. in height, and having an internal volume of about 540 cubic centims., was weighed, first empty, and subsequently when filled with distilled water at a known temperature. The necessary data were thus afforded for accurately determining its capacity at the temperature of the air. Molten silver was then poured into it, the temperature at the time of pouring being ascertained by the calorimetric method. The precautions, as regards filling, pointed out by Mr. Mallet, were adopted; and as soon as the metal was quite cold, the cone with its contents was again weighed.

Experiments were also made on the density of fluid bismuth; and two distinct determinations gave the following results:—

$$\left.\begin{matrix}10{\cdot}005\\10{\cdot}072\end{matrix}\right\} \text{ Mean } 10{\cdot}039.$$

The invention of the oncosimeter§ appeared to afford an opportunity for resuming the investigation on a new basis, more especially as the delicacy of the instrument had already

* Read February 12, 1881.

† Roberts, Proc. Roy. Soc. vol. xxiii. p. 493.

‡ Proc. Roy. Soc. vol. xxii. p. 366, and vol. xxiii. p. 209.

§ Wrightson, Journ. Iron and Steel Inst. No. II. 1879, p. 418.

been proved by experiments on a considerable scale for determining the density of fluid cast iron. The following is the principle on which this instrument acts.

If a spherical ball of any metal be plunged below the surface of a molten bath of the same or another metal, the cold ball will displace its own volume of molten metal. If the densities of the cold and molten metal be the same, there will be equilibrium, and no floating or sinking effect will be exhibited. If the density of the cold be greater than of the molten metal, there will be a sinking effect, and if less a floating effect, when first immersed. As the temperature of the submerged ball rises, the volume of the displaced liquid will increase or decrease according as the ball expands or contracts. In order to register these changes the ball is hung on a spiral spring, and the slightest change in buoyancy causes an elongation or contraction of this spring which can be read off on a scale of ounces, and is recorded by a pencil on a revolving drum. A diagram is thus traced out the ordinates of which represent increments of volume, or, in other words, of weight of fluid displaced—the zero-line, or line corresponding to a ball in a liquid of equal density, being previously traced out by revolving the drum without attaching the ball of metal itself to the spring, but with all other auxiliary attachments. By a simple adjustment the ball is kept constantly depressed to the same extent below the surface of the liquid; and the ordinate of this pencil-line, measuring from the line of equilibrium, thus gives an exact measure of the floating or sinking effect at every stage of temperature, from the cold solid to the state when the ball begins to melt.

If the weight and specific gravity of the ball be taken when cold, we have, with the ordinate on the diagram at the moment of immersion, sufficient data for determining the density of the fluid metal; for

$$\frac{W}{W'} = \frac{D}{D'},$$

the volumes being equal. And, remembering that

$$W \text{ (weight of liquid)} = W' \text{ (weight of ball)} + x$$

(where x is always measured as a $+$ve or $-$ve floating effect), we have

$$\therefore \quad D = \frac{D' \times (W' + x)}{W'}.$$

The following table shows the results of six experiments to determine the density of fluid bismuth made by the authors in the laboratory of the Royal Mint. The bismuth was kept just above its melting-point; and this was ensured by placing pieces of metal in the molten mass, which were observed just to melt.

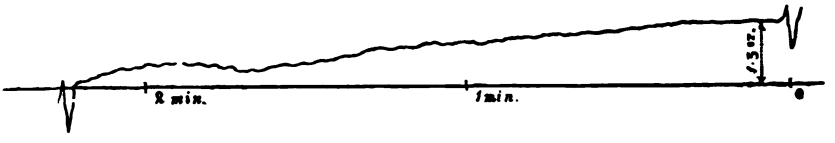
No. of exp.	Diameter of ball, in inches.	Weight, in troy ounces, including the stem for attachment.	Specific gravity of cold ball, including this stem.	Floating effect on first immersion, in troy ounces.	Deduced specific gravity of fluid metal.	Remarks.
1.	2	23·33	9·72	1·0	10·13	Bismuth ball in fluid bismuth.
2.	2·25	33·46	9·755	1·3	10 11	do.
3.	do.	33·37	9·757	0·6	9·94	do.
4.	do.	33·53	9·774	0·7	9·98	do.
5.	do.	22·184	6·99 (iron)	9·3	9·92	Iron ball in fluid bismuth.
6.	do.	22·184	7·02 (do.)	10·2	10·25	do.
					Mean ..... 10·055	
					Specific gravity of solid bismuth ..... 9·82	

It will be seen that, considering the difficulties of manipulation, the results are remarkably concordant, and their mean agrees very closely with that obtained by Mallet's method. We venture to think, therefore, that the density of bismuth in the solid and the fluid state may now be considered to be definitely settled.

Fig. 1 is the oncosimeter diagram of experiment No. 2 (see table), with a calculation of the fluid specific gravity annexed. When first immersed, the floating effect is 1·3 troy ounce, which (with the weight and density of the ball known) is all we require to determine the fluid-density. Bismuth has a low heat-conducting power; and therefore the mass of the ball is reduced by surface-melting before much heat can penetrate to

Fig. 1.

Oncosimeter Diagram of Bismuth Ball, 2·25 inches diameter, immersed in Fluid Bismuth (see table, Exp. 2).



Weight of ball and immersed part of stalk ..... 33·46 oz.
Specific gravity of do. do. ..... 9·755
First floating effect ..... 1·3 oz.

$$\text{Specific gravity of fluid} = \frac{34{\cdot}76 \times 9{\cdot}755}{33{\cdot}46} = 10{\cdot}11.$$

the centre. Hence the diagram does not accurately show, as in metals of high conducting-power, the change of volume, the effect being compounded with that produced by loss of mass.

In the case of iron, the conducting-power of which is high, diagrams taken with the oncosimeter show correctly the expansion of the ball until it is in a uniformly plastic state. Fig. 2 is a diagram of a cast-iron ball, 4 inches diameter, immersed in fluid iron of the same quality (No. 4 Cleveland). In this the solid iron is shown to be of less volume than the liquid for about 25 seconds, then to rise gradually in volume until in 4 minutes it becomes plastic (this having been proved by taking balls out in this stage of temperature, when an iron pin could be run through and through the metal as though it were a piece of putty). The slight fall of the line for about 2 minutes towards the left of the diagram probably shows a slight loss of mass owing to surface-melting; and then the whole ball melts with great rapidity, and as it joins the liquid metal of the bath the line of volume shoots rapidly down to the equilibrium-line. This diagram shows, up to the plastic point (where loss of mass commences), the gradual change of volume at progressive intervals of time.

The diagram read from left to right should represent the change from liquid to solid; and this is quite in accordance with other observations on cast iron*.

* Journ. Iron and Steel Inst. No. II. 1879, and No. I. 1880.

Fig. 2.

Experiment No. 23, on Iron.



Weight of ball and immersed part of stalk.....		132 oz.
Specific gravity of ball and immersed part of stalk		6·95
Maximum sinking effect.....		2 oz.
Maximum floating effect		11 oz.
Specific gravity of fluid iron	$= \frac{6\cdot95\times130\cdot0}{132}$ ...	$=6\cdot84$
Specific gravity of plastic metal	$= \frac{6\cdot95\times132}{145\cdot00}$ ...	$=6\cdot33$

4-inch ball of No. 4 foundry iron (Cleveland). Run with very hot metal. Immersed in No. 4 foundry iron.

According to these experiments, iron expands rapidly (as much as 6 per cent.) in cooling from the liquid to the plastic state, and then contracts 7 per cent. to solidity; whereas bismuth appears to expand in cooling from the liquid to the solid state about 2·35 per cent.

XXI. *An Integrating-Machine.*

By C. V. Boys, *Assoc. Royal School of Mines.**

[Plate XI.]

All the integrating-machines hitherto made of which I can find any record may be classed under two heads:—one, of which Amsler's beautiful instrument is the sole representative, depending on the revolution of a disk which partly rolls and partly slides on the paper; the other, comprising

* Read February 26, 1881.

all the remaining machines, depending on the varying diameters of the parts of a rolling system. As this subject has been treated so recently by Mr. Merrifield in his "Report on the Present State of Knowledge of the Application of Quadratures and Interpolation to Actual Data," read at the meeting of the British Association at Swansea, 1880, in which he briefly describes previous machines and refers to the papers in which a full description may be found, I do not think it advisable to say more concerning them, except that none of them do their work by the method of the mathematician, but in their own way. The machine, however, which I have the honour of bringing before the notice of the Physical Society is an exact mechanical translation of the mathematical method of integrating $y\,dx$, and thus forms a third type of instrument.

The mathematical rule may be described in words as follows:—Required the area between a curve, the axis of x, and two ordinates. It is necessary to draw a new curve such that its steepness, as measured by the tangent of the inclination, for any value of x may be proportional to the ordinate of the given curve for the same value of x. The *ascent* then made by the new curve in passing from one ordinate to the other is a measure of the area required.

On Plate XI. is a plan and side elevation of a model of the instrument made merely to test the idea: the arrangement of the details is not altogether convenient. The framework is a kind of T-square carrying a fixed centre B, which moves along the axis of x of the given curve; a rod passing always through B carries a pointer A, which is constrained to move in the vertical line $e\,e$ of the T-square; A then can be made to follow any given curve. The distance of B from the edge $e\,e$ is constant; call it k: therefore the inclination of the rod AB is such that its tangent is equal to the ordinate of the given curve divided by k; that is, the tangent of the inclination is proportional to the ordinate; therefore, as the instrument is moved over the paper, AB has always the inclination of the required curve.

The part of the instrument that draws the curve is a three-wheeled cart of lead whose front wheel F is mounted, not as a castor, but like the steering-wheel of a bicycle. When such a cart is moved, the front wheel F can only move in the

direction of its own plane, whatever be the position of the cart; if, therefore, the cart is so moved that F is always in the line *e e* and at the same time has its plane parallel to the rod A B, then F must necessarily describe the required curve; and if it is made to pass over a sheet of black tracing-paper, the required curve will be drawn.

The upper end of the T-square is raised above the paper, and forms a bridge, under which the cart travels. There is a longitudinal slot in this bridge, in which lies a horizontal wheel, carried by that part of the cart corresponding to the head of a bicycle; by this means the horizontal movement communicated to the front wheel of the cart by the bridge is equal to that of the pointer A; at the same time the cart is free to move vertically. It only remains to describe the mechanism which causes the plane of the front wheel of the cart to be always parallel to A B. For this purpose I make use of the principle of the epicyclic train. If three equal wheels are mounted on an arm, with their centres in a straight line and their edges in contact, any motion may be given to the arm or to the first wheel, *a*, yet lines on the first and last wheels, *a* and *b*, if ever parallel, will always be so. Instead of the middle wheel an open band may connect the two outside wheels, with the same result. In the same way another arm may carry a third wheel, *c*, connected with *b* by an open band, as shown; then whatever motion is given to the wheel *a* or to the arms, lines on *a* and *c*, if ever parallel, will always be so. To apply this principle the wheel *a* is mounted on the fixed centre B, and its rotation is equal to that of the rod A B. A pair of arms hinged at H connect B with that part of the cart corresponding to the head of a bicycle, while

Fig. 1.

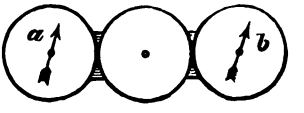
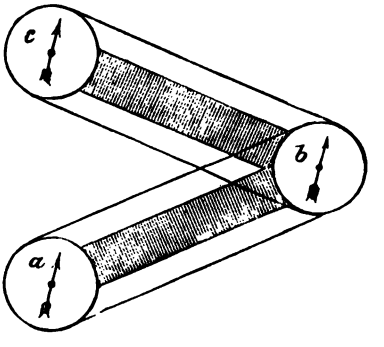


Fig. 2.



the handles are replaced by the wheel c; the wheel b is mounted on the hinge H, and a single band goes round all three wheels, as shown. The wheel b and the arms are balanced about B by the counterpoise W. Thus, as A traces out any given curve, the front wheel of the cart has its plane always parallel to A B; and as the connexion between the cart and B in no way interferes with its vertical motion, the front wheel must describe the required curve. As the ascent in this curve is equal to $\frac{1}{k}\int y\,dx$, all that has to be done is to measure the ascent, multiply by k, and the product is the area required. If A is taken round any closed curve, the ascent can be measured immediately by a rule and multiplied by k as before.

In the instrument shown, k can be made either one, two, three, π, or $\frac{\pi}{2}$ inches. If the one-inch constant is used, the inclination of the rod A B is with large ordinates so great and the motion of the cart so nearly at right angles to the direction in which it is pushed, that there is danger of its being upset. This difficulty is in great measure avoided by inclining the board in the direction $e\,e$; and then, as the inclination of A B becomes greater and the power of the instrument to drive the cart becomes less, the action of gravity on the cart increases, and it can be moved with equal ease in all directions.

As the model works exceedingly well, I have no doubt that a carefully-made machine would give results as accurate as any other planimeter. As an aid in teaching physics to pupils not familiar with the principles of the integral calculus, and in illustrating those principles themselves, I think it would be found of very great value. To justify myself for bringing a subject purely mathematical before this Society, I will briefly give a few examples of its use. For simplicity's sake let $k=1$.

If A is moved along the axis of x (that is, $y=0$), the cart draws a horizontal line, the ascent is nothing, and the area is nothing. By this means any want of parallelism between the front wheel F and A B can be detected and set right (see Plate XI. fig. 1).

If A is moved along a line parallel to the axis of x (that is, $y=c$), the cart draws the straight line $y=cx$; that is, the

inclination is constant, showing that area is passed over uniformly (see Plate XI. fig. 1).

If A is moved along an inclined straight line $y=cx$, the cart draws the parabola $y=\frac{cx}{2}$ (see Plate XI. fig. 2). This is the path of a projectile: and the machine proves that it must be so; for taking abscissæ as time, the curve representing the velocity of falling is an inclined straight line, while the space fallen in any time, being measured by the area between the inclined line and the axis of x up to that point, is found by the cart; and as the horizontal movement is proportional to the time, the curve drawn by the cart is the path of a projectile.

If A is moved along the curve $y=\frac{1}{x^2}$, a curve representing attraction, the cart draws a rectangular hyperbola, showing that potential varies inversely as distance. As abscissæ are distances and ordinates forces, it is plain that the work done by an attracting body in bringing a unit from an infinite distance up to a point (that is, the potential at that point) is measured by the area between the curve, the axis of x, and the ordinate at that point; and as in finding this area the machine draws a rectangular hyperbola in which, of course, y varies inversely as x, it proves that potential varies inversely as distance (see Plate XI. fig. 3).

If A is moved along the logarithmic curve $y=e^x$, the cart draws an identical curve; and this it should do, since $\frac{de}{dx}=e^x$ (see Plate XI. fig. 4). Since the pointer A and the cart describe identical curves, it is plain that their distance asunder is constant; if, therefore, these two are connected by a link, and then the machine is started on the axis of x, they will each describe a horizontal line. But this will be an unstable motion; for if they depart ever so little from horizontal motion, they will turn aside faster and faster, the cart pulling the pointer and the pointer directing the cart, and thus originate the logarithmic curve.

If A is moved along a wave-line symmetrically placed with respect to the axis of x, the cart draws another wave-line a quarter of a wave-length behind the first in point of time. If

the first line represents the varying strength of an induced electrical current, the second shows the nature of the primary that would give rise to such a current (see Plate XI. fig. 5).

Fig. 6 shows the application of the machine to the determination of the area of a closed curve.

The rules for finding maxima and minima and points of inflexion are rendered obvious by manipulating the machine. By no means can the cart be made to trace a maximum or a minimum unless the pointer A *cross* the axis of x; nor can it pass a point of inflexion unless A pass a maximum or a minimum.

An indefinite integral requires the addition of a constant; but on integrating between limits this constant goes out. This is illustrated by the fact that the cart may be started on any level on the board, but the ascent made is the same.

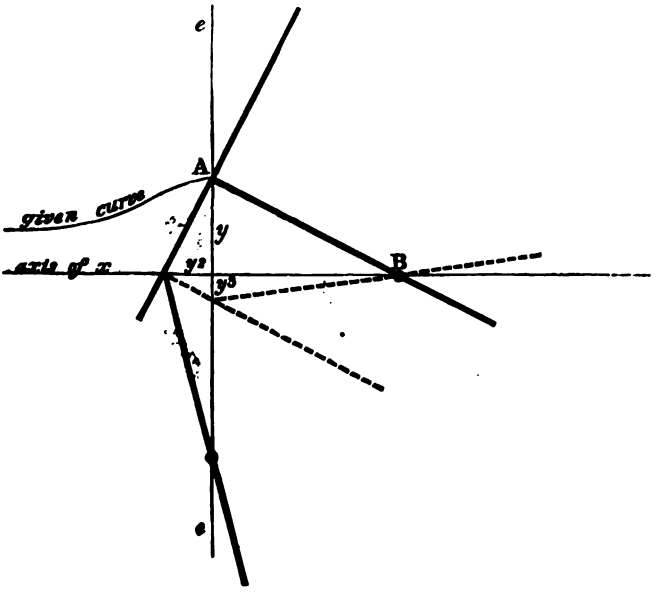
Not only does the machine integrate $y\,dx$, but if the plane of the front wheel of the cart is set at right angles instead of parallel to AB, then the cart finds the integral of $\frac{dx}{y}$, and thus solves problems such, for instance, as the time occupied by a body in moving along a path when the law of the velocity at different parts is known. This is evidently true; for if a line be drawn perpendicularly to AB through B, it will cut $e\,e$ at a point distant from the axis of x by an amount equal to $\frac{1}{y}$, and therefore its inclination is such that its tangent is equal to $\frac{1}{y}$. As the cart travels down instead of up for positive values of y, its descent instead of its ascent must be taken.

Some modifications in the instrument would enable it to integrate y^2dx or y^3dx; it could also be made to integrate the product of two or more functions. I do not intend to go into details with regard to these extensions of the machine, but merely to explain the principle that would be employed. As before, let $k=1$. To integrate y^2dx the rod AB would be replaced by a T, as shown in fig. 3. The head of this would obviously cut the axis of x in advance of the edge $e\,e$ by an amount equal to y^2. Let a rod pass through this point of intersection and through a point on $e\,e$ distant from the

axis of x by an amount equal to k or 1, then the angle between this rod and $e\,e$ is such that its tangent is equal to y^2; and if the plane of the front wheel of the cart be kept at right angles to this rod, the cart will integrate y^2dx.

To integrate y^3dx the second rod would be kept parallel to A B, and the point where it cut $e\,e$ would be distant from the axis of x by an amount equal to y^3. If then the plane of the front wheel of the cart were kept parallel to the line connecting this point with B, as shown by the dotted

Fig. 3.



lines in fig. 3, the machine would integrate y^3dx. In these cases, as in the integration of products, it would be well to make k so large that the ordinates should never much exceed it.

To integrate the product of two functions—that is, to find $\int \phi x\, \psi x\, dx$, the two curves $y=\phi x$ and $y=\psi x$ would have to be drawn about two axes of x, one above the other, and two tracing-points, each on the line $e\,e$, would follow the curves. The fixed centre B would pass over the lower axis of x; but the epicyclic connexion, instead of joining B with the cart,

would connect B with the upper tracing-point, and cause a rod passing through this point to be always at right angles to A B. This upper rod would cut the upper axis of x at a point distant from $e\,e$ by an amount equal to $\phi x\,\psi x$; if, then, the front wheel of the cart is kept at right angles to a line joining this point of intersection with a point on $e\,e$ distant from the upper axis of x by an amount equal to k or 1, then the cart will draw the line $y=\int_0^x \phi x\,\psi x\,dx$. The same principle might be applied to integrate the product of more than two functions.

As in the case of simple functions, so with squares, cubes, and products, the reciprocal could be integrated by twisting the plane of the front wheel of the cart through a right angle. Also the integral of $\frac{\phi x}{\psi x}$ could be found by making the lower curve $y=\psi x$, the upper curve $y=\phi x$, and by keeping the rod which passes through the upper tracing-point parallel instead of at right angles to A B.

The axis of x is drawn by using a little T square of such a length that its end is the same distance from the edge of the board as the fixed centre B; then a pencil held at the end while the square is moved across the board will at once give the axis of x.

I do not consider the modifications of the machine to be of much importance; but the simple machine as described in the first part of this paper, is, I think, interesting as being the only one that really illustrates the mathematical formula for the integration of $y\,dx$.

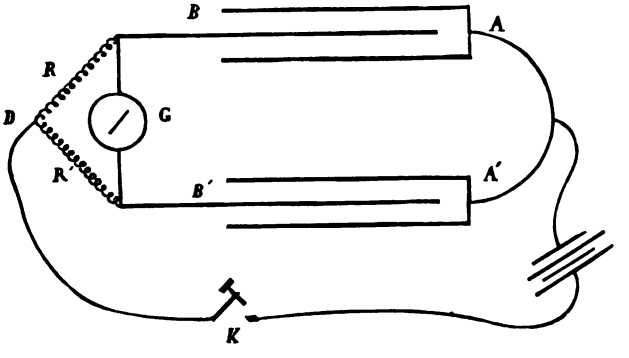
My thanks are due to Mr. Hilger, of Tottenham Court Road, for the great care and skill which he has bestowed upon the construction of the instrument. Certain modifications of detail, however, have been introduced which make it more easy of manipulation without sacrifice of simplicity.

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South Kensington.

XXII. *On a Method of Comparing the Electrical Capacities of two Condensers.* *By* R. T. Glazebrook, *M.A., Fellow of Trinity College, and Demonstrator of Experimental Physics at the Cavendish Laboratory, Cambridge* *.

The following is a well-known method of comparing the capacities of two condensers:—

Let A, A′ be the outer coatings, B, B′ the inner of two condensers. Connect A A′ together, and to one pole of a battery. Connect B to a resistance R and to one pole of a



galvanometer, B′ to another resistance R′ and to the other pole of the galvanometer. Connect the other ends of R R′ together and to a key K, and let the second screw of the key be in connexion with the other pole of the battery. Let C C′ be the capacities of the condensers. On depressing the key the condensers are charged; and it is easy to show that, if $CR = C'R'$, no current passes through the galvanometer.

If, then, we adjust R until no current is observed on making contact, R′ remaining unaltered, we can find the ratio of C to C′.

I propose to discuss the more general problem of finding the current through the galvanometer when the equation $CR = C'R'$ is not fulfilled, and hence to obtain the conditions of sensibility.

Let V_1 be the potential of A, V_2 of the other pole of the battery, V of B, V′ of B′, at time t. Let G be the galvanometer resistance.

* Read January 22, 1881.

Let ι = current in R;
ι' = „ R′;
ι_1 = current into condenser A;
ι_1' = „ „ B;
x = current through galvanometer;
Q, Q' = the quantities in the condensers.

Let us further suppose that there is a small leakage through the condensers, $\rho\rho'$ being their resistances.

Then we have

$$\left.\begin{aligned} \iota &= \frac{V_2-V}{R}, \quad \iota'=\frac{V_2-V'}{R'}, \quad x=\frac{V-V'}{G}, \\ \iota_1 &= \iota-x, \quad \iota_1'=\iota'+x, \\ Q &= C(V-V_1), \quad Q'=C'(V'-V_1), \\ \iota_1 &= \frac{dQ}{dt}+\frac{V-V_1}{\rho}, \\ \iota_1' &= \frac{dQ'}{dt}+\frac{V'-V_1}{\rho'}, \end{aligned}\right\} \quad . \quad . \quad (1)$$

From these we obtain:—

$$G x+R\iota-R'\iota'=0; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$CR\frac{d\iota}{dt}+\frac{R+\rho}{\rho}\left\{\iota-\frac{V_2-V_1}{R+\rho}\right\}-x=0; \quad . \quad . \quad (3)$$

$$C'R'\frac{d\iota'}{dt}+\frac{R'+\rho'}{\rho'}\left(\iota'-\frac{V_2-V_1}{R'+\rho'}\right)+x=0. \quad . \quad . \quad . \quad (4)$$

Assume

$$\begin{aligned} \iota-\frac{V_2-V_1}{R+\rho} &= Ae^{-nt}, \\ \iota'-\frac{V_2-V_1}{R'+\rho'} &= A'e^{-nt}, \\ x &= Be^{-nt}. \end{aligned}$$

On substituting we have

$$A\left\{\frac{R+\rho}{\rho}-CRn\right\}-B=0, \quad . \quad . \quad . \quad . \quad (5)$$

$$A'\left\{\frac{R'+\rho'}{\rho'}-C'R'n\right\}+B=0, \quad . \quad . \quad . \quad (6)$$

$$GB+RA-R'A'=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

whence

$$\left.\begin{aligned} A\left\{G\left(\frac{R+\rho}{\rho}-RCn\right)+R\right\}-R'A'=0,\\ A'\left\{G\left(\frac{R'+\rho'}{\rho'}-R'C'n\right)+R'\right\}-RA=0.\end{aligned}\right\} \quad . \quad (8)$$

Eliminating $A\,A'$ we arrive at the quadratic,

$$\begin{aligned} n^2-n\left\{\frac{1}{G}\left(\frac{1}{C}+\frac{1}{C'}\right)+\frac{1}{R'C'}\left(\frac{R+\rho}{\rho}\right)+\frac{1}{RC}\frac{R'+\rho'}{\rho'}\right)\right\}\\ +\frac{1}{GRR'CC'}\left\{\frac{G(R+\rho)(R'+\rho')}{\rho\rho'}+\frac{R(R'+\rho')}{\rho'}\right.\\ \left.+\frac{R'(R+\rho)}{\rho}\right\}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)\end{aligned}$$

Let n_1 n_2 be the roots, and let

$$\left.\begin{aligned} G\left(\frac{R+\rho}{\rho}-RCn\right)+R=\lambda,\\ G\left(\frac{R'+\rho'}{\rho'}-R'Cn\right)+R'=\lambda'.\end{aligned}\right\} \quad . \quad (10)$$

Then from (8) we have

$$\left.\begin{aligned} \lambda_1A_1+\lambda_2A_2 &= R'(A_1'+A_2'),\\ \lambda_1'A_1'+\lambda_2'A_2' &= R(A_1+A_2),\end{aligned}\right\} \quad . \quad . \quad (11)$$

where A_1, λ_1 &c. denote the values of A, λ corresponding to n_1, n_2.

Also initially

$$\iota=\frac{V_2-V_1}{R}, \quad \iota'=\frac{V_2-V_1}{R'}; \quad . \quad . \quad . \quad . \quad (12)$$

Therefore, putting $t=0$ and $V_2-V_1=E$ in the equations

$$\iota=\frac{V_2-V_1}{R+\rho}+A_1e^{-n_1t}+A_2e^{-n_2t}$$

$$\iota'=\frac{V_2-V_1}{R'+\rho'}+A_1'e^{-n_1t}+A_2'e^{-n_2t},$$

we find

$$\left.\begin{aligned} A_1+A_2 &= \frac{E\rho}{R(R+\rho)},\\ A_1'+A_2' &= \frac{E\rho'}{R'(R'+\rho')}.\end{aligned}\right\} \quad . \quad . \quad . \quad (13)$$

Solving for $A_1 A_2$, we get

$$A_1=\frac{E}{R(n_1-n_2)}\left\{\frac{1}{GC}\left(\frac{\rho}{R+\rho}+\frac{\rho'}{R'+\rho'}\right)+\frac{1}{R}\left(\frac{1}{RC}-\frac{n_2\rho}{R+\rho}\right)\right\}, \quad \ldots\ldots\ldots \quad (14)$$

$$A_2=-\frac{E}{R(n_1-n_2)}\left\{\frac{1}{GC}\left(\frac{\rho}{R+\rho}-\frac{\rho'}{R'+\rho'}\right)+\frac{1}{R}\left(\frac{1}{RC}-\frac{n_1\rho}{R+\rho}\right)\right\}, \quad \ldots\ldots\ldots \quad (15)$$

and similar values for $A_1' A_2'$.

Hence we find

$$\begin{aligned}Gx=E&\left\{\frac{R'}{R'+\rho'}-\frac{R}{R+\rho}\right\}\\&+\frac{E}{n_1-n_2}\left[\left(\frac{1}{R'C'}-\frac{1}{RC}\right)(e^{-n_1t}-e^{-n_2t})\right.\\&+\left\{\left(n_2-\frac{1}{GC}-\frac{1}{GC'}\right)e^{-n_1t}-\left(n_1-\frac{1}{GC}-\frac{1}{GC'}\right)e^{-n_2t}\right\}\\&\left.\times\left\{\frac{\rho}{R+\rho}-\frac{\rho'}{R'+\rho'}\right\}\right]. \quad \ldots\ldots\ldots \quad (16)\end{aligned}$$

Let us take the case in which there is no leakage first, $\rho=\rho'=\infty$, and

$$x=\frac{E}{G(n_1-n_2)}\left(\frac{1}{R'C'}-\frac{1}{RC}\right)(e^{-n_1t}-e^{-n_2t}). \quad \ldots \quad (17)$$

Thus, if $RC=R'C'$, we see that x is zero for all values of t.

The total effect on the galvanometer, since the time of charging is short, is proportional to the quantity of electricity which passes. To find this we integrate the value of x with respect to t from 0 to τ, and suppose τ so large that

$$e^{-n_1\tau}=e^{-n_2}=0.$$

Then, if P be the quantity,

$$P=\frac{E(R'C'-RC)}{GRR'CC'n_1n_2};$$

also

$$n_1n_2=\frac{G+R+R'}{GRR'CC'};$$

$$\therefore \quad P=\frac{E(R'C'-RC)}{G+R+R'}; \quad \ldots\ldots \quad (18)$$

and if H be the strength of the field in which the needle hangs, T the time of a complete oscillation, k the galvanometer-constant, and α the angle through which the needle is turned,

$$P = \frac{HT}{\pi k} \sin\frac{\alpha}{2};$$

$$\therefore \quad \sin\frac{\alpha}{2} = \frac{\pi k}{HT} \cdot \frac{E(R'C' - RC)}{(G+R+R')}, \quad . \quad . \quad . \quad (19)$$

which leads to the condition that, when there is no throw of the galvanometer, $R'C' = RC$.

We proceed to inquire what resistances will give the most accurate value for the capacity C in terms of C′, the known capacity of a standard condenser when using a given galvanometer. Let us suppose the adjustment made by varying R, and determine the error δa produced in α by an error δR in R. Then, remembering that, when the adjustment is perfect, $RC = R'C'$ and $\alpha = 0$, if δR is the error from perfect adjustment, we have

$$\delta a = -\frac{2}{HT} \frac{E\pi k C \delta R}{(G+R+R')}; \quad . \quad . \quad . \quad . \quad (20)$$

and if δC is the error in the capacity, since $C = \frac{R'C'}{R}$,

$$\delta C = -\frac{R'C'\delta R}{R^2} = \frac{HT(G+R+R')R'C'}{2E\pi k C R^2} \delta a;$$

or, since $CR = C'R'$,

$$\delta C = \frac{HT(G+R+R')}{2E\pi k R} \delta a. \quad . \quad . \quad . \quad . \quad (21)$$

Now k varies as the number of turns in the galvanometer, and so also does G;

$$\therefore \quad K = \mu G,$$

$$\therefore \quad \delta C = \frac{HT\delta a}{2E\pi\mu} \left\{ \frac{1}{G} + \frac{1}{R} + \frac{R'}{GR} \right\}; \quad . \quad . \quad (22)$$

and if we suppose that we are liable to an error δa in α, the error in C is least when the resistances R and R′ are both high.

Thus it is best to use, with a given galvanometer, high resistances R and R′.

We arrive at the same result if we make the adjustments by varying R′ instead of R.

Again, let us suppose that we have a galvanometer with a given channel, and we wish to fill it with wire so as to be most sensitive. Let V be the volume of the channel, y the radius of the wire, l its length, ρ its specific resistance, and suppose we neglect the thickness of the covering; then

$$4\rho y^2 = V,$$

$$G = \frac{\rho l}{\pi y^2} = \frac{4\rho l^2}{V},$$

$$k = g\rho,$$

where g depends only on the form and dimensions of the channel. We must therefore make

$$\frac{\frac{4\rho l^2}{V} + R + R'}{l}$$

a minimum. We find

$$\frac{4\rho}{V} - \frac{R+R'}{l^2} = 0; \quad \ldots\ldots \quad (23)$$

and we get finally

$$G = R + R'.$$

Now for a given value of G, R and R′ must be as high as possible; therefore we must make the resistance of our galvanometer as high as possible.

Returning to the general case in which there is a leakage in the condensers, and putting $t = \tau$, τ being so large that the terms involving $e^{-m\tau}$ may be neglected, we get

$$x = \frac{E}{G}\left\{\frac{R'}{R'+\rho'} - \frac{R}{R+\rho}\right\}. \quad \ldots\ldots \quad (24)$$

Thus there is a steady current through the galvanometer, and the needle is permanently deflected.

Again, if $t = 0$, $x = 0$. But let us suppose t very small, so that, on expanding e^{-mt}, powers higher than the first may be neglected, and find the initial current. We find

$$x = \frac{E}{G}\left\{\frac{R'C' - RC}{RC\,R'C'} + \frac{1}{G}\left(\frac{1}{C} + \frac{1}{C'}\right)\left(\frac{\rho}{R+\rho} - \frac{\rho'}{R'+\rho'}\right)\right\}t, \quad (25)$$

which reduces, if we neglect powers of $\frac{1}{\rho}$ above the first, to

$$x = \frac{E}{G}\left\{\frac{R'C' - RC}{RC\,R'C'} + \frac{1}{G}\left(\frac{1}{C} + \frac{1}{C'}\right)\left(\frac{R'}{\rho'} - \frac{R}{\rho}\right)\right\}t. \quad (26)$$

By altering R the sign of this may be made to change, and thus the initial current may be in the same or in the opposite direction to the final. In practice this is indicated by a short kick of the needle in one direction, followed by a deflection in the other.

On the same assumptions as to ρ, ρ', let us find the quantity of electricity which passes through the galvanometer in time τ, τ being very short, but yet so long that $e^{-n\tau}$ may be neglected. Integrating (16) and calling the quantity P, we have

$$P=\frac{E}{G+R+R'}\left[\{R'C'-RC\}\left\{1-\frac{G\left(\frac{R}{\rho}+\frac{R'}{\rho'}\right)+RR'\left(\frac{1}{\rho}+\frac{1}{\rho'}\right)}{G+R+R'}\right\}\right.$$
$$\left.-\left\{\frac{R'}{\rho'}-\frac{R}{\rho}\right\}\{RC+R'C'\}\right]+\frac{E}{G}\left(\frac{R'}{\rho'}-\frac{R}{\rho}\right)\tau. \quad . \quad (27)$$

If τ be very short, we may neglect the last term compared with the others, and, to the same degree of approximation with respect to ρ ρ, we get as the condition of no kick,

$$R'C'-RC=\left(\frac{R'}{\rho'}-\frac{R}{\rho}\right)(R'C'+RC),$$

or

$$\frac{RC}{R'C'}=1-2\left(\frac{R'}{\rho'}-\frac{R}{\rho}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Again, let k, as before, be the galvanometer-constant, and δ the permanent deflexion. Then, from (25),

$$\frac{E}{G}\left\{\frac{R'}{\rho'}-\frac{R}{\rho}\right\}=k\tan\delta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

$$\frac{RC}{R'C'}=1-\frac{2Gk}{E}\tan\delta; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

and this equation enables us to determine the capacity.

Let us suppose the adjustment made by varying R. Then, starting from a position in which the first kick is in an opposite direction to the final deflexion, adjust R until that kick is just reduced to zero, and the spot of light moves off gradually in the one direction, and after some oscillations comes to rest. Then, if δ is the deflexion of the galvanometer-needle the capacity is

$$C=\frac{C'R'}{R}\left\{1-\frac{2Gk}{E}\tan\delta\right\}.$$

Unless the leakage is considerable, the correction will be very small.

In measuring the capacity of many condensers, the difficulty is increased by the phenomenon of electric absorption. In fact the condenser has no true capacity; for the charge produced by a given electromotive force depends on the time during which that force has acted. We may, however, take the capacity as the ratio of the instantaneous charge to the electromotive force producing it; and in this case (contact with the battery being maintained only for a very short time) we may perhaps look on electric absorption as a kind of conduction through the substance of the condenser. We must suppose that the resistance to the conduction is a function of the time, which becomes indefinitely great after a not very long interval, but which we may perhaps treat as sensibly constant during the time for which contact is maintained; and if ρ_0, ρ'_0 be the values of this resistance during that interval, and, as before, we may neglect $\frac{1}{\rho_0^2}$ &c. and higher powers, we have, as the value of the capacity,

$$C = \frac{R'C'}{R}\left\{1 - 2\left(\frac{R'}{\rho'_0} - \frac{R}{\rho_0}\right)\right\}.$$

Thus a small correction should be applied to the value $\frac{R'C'}{R}$, depending on the rate of absorption during the interval for which contact is maintained with the battery. An approximation to this quantity may be obtained by charging the condenser for some time with a battery of known electromotive force, and then allowing it to discharge itself at small intervals of time through the galvanometer. On the whole, however, the results of measurements made, neglecting this correction, are fairly satisfactory.

The capacity of a paraffin condenser was determined by several observers during the past term at the Cavendish Laboratory. Their results differed by from $\frac{2}{3}$ to 1 per cent. The standard used was not in all cases the same; and the measures obtained by one observer, comparing this same condenser with two different standards, differed by about $\frac{1}{3}$ per cent. It seemed possible to determine within 10 ohms, when each of the resistances R, R′ was about 5000 ohms, the value of R for which the initial kick was zero.

XXIII. *Electric Absorption of Crystals.* *By* H. A. Rowland *and* E. H. Nichols, *of the Johns Hopkins University, Baltimore* *.

[Plate XII.]

I.

The theory of electric absorption does not seem to have as yet attracted the general attention which its importance demands; and from the writings of many physicists we should gather the impression that the subject is not thoroughly understood. Nevertheless the subject has been reduced to mathematics; and a more or less complete theory of it has been in existence for many years. Clausius seems to have been the first to give what is now considered the best theory. His memoir, "On the Mechanical Equivalent of an Electric Discharge," &c., was read at the Berlin Academy in 1852†. In an addition to this memoir in 1866 he shows that a dielectric medium having in its mass particles imperfectly conducting would have the property of electric absorption. Maxwell, in his 'Electricity,' art. 325, gives this theory in a somewhat different form, and shows that a body composed of layers of different substances would possess the property in question. One of us, in a note in the 'American Journal of Mathematics,' No. 1, 1878, put the matter in a somewhat different form, and investigated the conditions for there being no electric absorption.

All these theories agree in showing that there should be no electric absorption in a perfectly homogeneous medium. A mass of glass can hardly be regarded as homogeneous, seeing that when we keep it melted for a long time a portion separates out in crystals. Glass can thus be roughly regarded as a mass of crystals with their axes in different directions in a medium of a different nature. It should thus have electric absorption. Among all solid bodies, we can select

* Read May 14th, 1881.

† I have obtained my knowledge of this memoir from the French translation, entitled *Théorie Mécanique de la Chaleur*, par R. Clausius, translated into French by F. Folie: Paris, 1869. The "Addition" does not appear in the memoir published in Pogg. *Ann.* vol. lxxxvi. p. 337, but was added in 1866 to the collection of memoirs.

none which we can regard as perfectly homogeneous along any given line through them, except crystals. The theory would then indicate that crystals should have no electric absorption; and it is the object of this paper to test this point. The theory of both Clausius and Maxwell refers only to the case of a condenser made of two parallel planes. In the "Note" referred to, one of us has shown that in other forms of condenser there can be electric absorption even in the case of homogeneous bodies. Hence the problem was to test the electric absorption of a crystal, in the case of an infinite plate of crystal with parallel sides. The considerations with regard to the infinite plate were avoided by using the guard-ring principle of Thomson.

The crystals which could be obtained in large and perfect plates were quartz and calcite. These were of a rather irregular form, about 35 millim. across and 1½ millim. thick, and perfectly ground to plane parallel faces. There were two quartz plates cut from the same crystal perpendicular to the axis, and two cleavage-plates of Iceland spar. There were also several specimens of glass ground to the same thickness; the plates were all perfectly transparent, with polished faces. Examined by polarized light, the quartz plates seemed perfectly homogeneous at all points except near the edge of one of them. This one showed traces of amethystine structure at that point; and a portion of one edge had a piece of quartz of opposite rotation set in; but the portion which was used in the experiment was apparently perfectly regular in structure. The fact that there are two species of quartz, right- and left-handed, with only a slight change in their crystalline structure, and that, as in amethyst, they often occur together, makes it not improbable that most pieces of right-handed quartz contain some molecules of left-handed quartz, and *vice versâ*. In this case quartz might possess the property of electric absorption to some degree. But Iceland spar should evidently more nearly satisfy the conditions. It is unfortunate that the two pieces of quartz were not cut from different crystals.

This reasoning was confirmed by the experiments, which showed that the quartz had about one ninth the absorption of glass; but that the Iceland spar had *none* whatever, and is

thus the first solid so far found having no electric absorption. Some crystals of mica &c. were tried; but calc spar is the only one which we can say, *à priori*, is perfectly homogeneous. Thus mica and selenite are so very lamellar in their character, that few specimens ever appear in which the laminæ are not more or less separated from one another; and thus they should have electric absorption.

II.

In the ordinary method of experimenting with the various forms of Leyden jar, there are, besides the residual discharge due to electric absorption in the substance of the insulator, two other sources of a return charge. The surface of the glass being more or less conducting, an electric charge creeps over the surface from the edges of the tinfoil. In discharging the jar in the usual way by a connecting wire, this surface remains charged, and the electricity is gradually conducted back to the coatings, and thus recharges them. If, furthermore, the coatings be fastened to the glass with shellac or other cement, the return charge may be partly due to it; for we have between the coatings not merely glass, but layers of glass, cement, &c., which the theory shows to give a residual discharge. Besides the coatings are not planes; and hence, as one of us has shown, there may be a return charge, even if the glass gave none between infinite planes. If the plates were merely laid on the glass without cementing, the same result would follow, since the insulator would then consist of air and glass in layers.

In the present research these were sources of error to be avoided, since the residual discharge due to the insulating plates themselves were to be compared. The condenser-plates were copper disks. These were amalgamated, so that there was a layer of mercury between them and the dielectric, which excluded the air and conducted the electricity directly to the surface of the dielectric: thus the condition of a single substance between the plates was fulfilled. The errors due to the creeping of the charge over the surface of the dielectric and that due to the plates not being infinite were avoided, the first entirely and the second partially, by the use of the guard-ring principle of Sir Wm. Thomson.

Fig. 1 (Pl. XII.) represents this apparatus. The plate of crystal, *c*, was placed between two amalgamated plates of copper, *a* and *b*, over the upper one of which the guard-ring, *d*, was carefully fitted; this ring, when down, served to charge and discharge the surface around the plate, *a*; and so the errors above referred to from the creeping of the charge along the plate, and from the plate not being infinite, were avoided.

The charging battery consisted of six large Leyden jars of nearly a square foot of coated surface each, charged to a small potential. Although accurate instruments were at hand for measuring the potential in absolute measure, it was considered sufficient to use a Harris unit-jar for giving a definite charge; for very accurate measurements were not desired, and the Harris unit-jar was entirely sufficient for the purpose. The return charge was measured by a Thomson quadrant-electrometer of the original well-known form.

The apparatus shown in fig. 1 performs all the necessary operations by a half turn of the handle *e*. By two half turns of the handle, one forward and the other back, the crystal condenser could be successively charged from the Leyden battery, discharged, the guard-ring raised, the upper plate, *a*, again insulated, and the connexion made with the quadrant-electrometer.

The copper ring, *d*, was suspended by three silk threads from the brass disk, *f*, which in turn could be raised and lowered by the crank, *g*. A small wire connected the ring with the rod on which was the ball *h*. This rod was insulated by the glass tube *i*, and could revolve about an axis at *k*. By the up-and-down motion of the rod the ball came into contact with the ball (*l*) connected with the earth, or the ball (*m*) connected with the battery. When the cranks were in the position shown in the figure, the heavy ball *n* caused the ball *h* to rise and press against *l*; but when *f* descended, the piece *o* pressed on the rod and caused *h* to fall on *m*.

Another rod, *q*, also more than balanced by a ball, *r*, was insulated by a glass tube, *s*, and connected with the quadrant-electrometer by a very fine wire. It could also turn around a pivot at *t*; so that when the ring *u* rested upon it, it fell on the upper condenser-plate *a*, and connected it with the electrometer: when the weight *u* was raised by the crank *v*,

the rod rested against *f*, and so connected the electrometer to the earth, to which the other quadrants were already connected.

At the beginning of an experiment, the insulating plate to be tested having been placed between the condenser-plates *a* and *b*, the handle was brought into such a position that the ring, *d*, rested on the plate around *a*. The lengths of the threads between *d* and *f* were such that *o* for this position of the handle did not touch *w*, and so *h* remained in connexion with the earth; and so *d* was also connected with the earth, and thus also with *b*. On now turning the handle further, the ball *h* descended to the ball *m*, and thus charged the condenser for any time desired. On now reversing the motion, the following operations took place:—

First, the ball *h* rose and discharged the condenser.

Second, the guard-ring *d* ascended.

Third, the rod *q*, which had been previously in contact with *p*, thus bringing the quadrant-electrometer to zero, now moved down and rested on the upper condenser-plate *a*. Thus any return charge quickly showed itself on the electrometer. The amount of deflection of the instrument depends upon the character of the dielectric, its thickness, the charge of the battery, the time of contact with the battery, and upon the length of time of discharging.

III.

In comparing the glass with the crystal plates, the electrometer was rendered as little sensitive as the ordinary arrangement of the instrument without the inductor-plate would allow. The electric absorption of the glass plates for a charge in the battery of two or three sparks from the Harris unit-jar then sufficed, after 20 or 30 seconds contact with the battery and 5 seconds discharging time, to give a deflection of about 200 scale-divisions, which were millimetres. The quartz and calcite plates were then alternately substituted for the glass, the same charge and the same intervals of contact being used, and the resulting deflections noted—two plates of each substance of the same thickness being used.

The results of the measurements are given in the following Tables, the effect of the glass being called 100.

TABLE I.

(*a*).

April 12, 1880.
Charge of battery, 2 sparks.
Contact 30 seconds.

Glass (1st plate)	100·0
Quartz (1st plate)	17·1
„ (2nd plate)	20·0
Calcite (1st plate)	0·0
„ (2nd plate)	0·0

(*b*).

April 13, 1880.
Charge of battery, 3 sparks.
Contact 20 seconds.

Glass (1st plate)	100·0
Quartz (1st plate)	19·3
Calcite (1st plate)	0·0

(*c*).

April 14, 1880.
Charge 3 sparks.
Contact 10 seconds.
Plates carefully dried by being in desiccator over night.

Glass (1st plate)	100·0
Quartz (1st plate)	10·7
Calcite (1st plate)	0·0

(*d*).

April 22, 1880.
Charge 2 sparks.
Contact 30 seconds.
Plate in desiccator since April 14.

Glass (2nd plate)	100·0
„ (1st plate)	96·3
Quartz (1st plate)	13·4
„ (2nd plate)	12·1
Calcite (1st plate)	0·0
„ (2nd plate)	0·0

TABLE II.

May 1. Relative Effects for different Intensities of Charge and Time of Contact.

Charge of battery.	Material.	Deflections, in millimetres.		
		Contact 5 seconds.	Contact 10 seconds.	Contact 20 seconds.
One spark	Glass (1st)	133·0	189·3	225·0
	Quartz (1st)	13·0	22·7	34·3
	Calcite (1st)	0·0	0·0	0·0
Two sparks	Glass (1st)	Off the scale	Off the scale	Off the scale
	Quartz (1st)	24·0	35·0	50·0
	Calcite (1st)	0·0	0·0	0·0

These Tables seem to prove beyond question that calcite in clear crystal has no electric absorption. Quartz seems to have about $\frac{1}{3}$ that of glass; but we have remarked that quartz is not a good substance to test the theory upon.

Some experiments were made with cleavage-plates of selenite, which are always more or less imperfect, as the laminæ are very apt to separate. These gave, however, effects about $\frac{1}{2}$ or $\frac{1}{4}$ those of glass.

In order to test still further the absence of electric absorption in calcite, the electrometer was rendered very sensitive, and the calcite plates were tested with gradually increasing

charges, from that which in glass gave 200 millim. after 1 second contact, up to the maximum charge (ten sparks of the unit-jar) which the condensers were capable of carrying. In these trials, the calcite still showed no effect, even with 30 seconds contact. During these experiments glass was frequently substituted for the calcite, to leave no question but that the apparatus was in working order.

It is to be noted that the relative effects of the quartz and the glass were different for dried plates and plates exposed to the atmosphere. This was possibly due to the glass being a better insulator, and thus retaining its charge better when dry than in its ordinary condition.

IV.

Thus we have found, for the first time, a solid which has no electric absorption; and it is a body which, above all others, the theory of Clausius and Maxwell would indicate. The small amount of the effect in quartz and selenite also confirms the theory, provided that we can show that in the given piece of quartz some molecules of right-handed quartz were mixed with the left; for we know that the theoretical conditions for the absence of electric absorption are rarely satisfied by laminated substances like selenite or mica. If the theory is confirmed, the apparatus here described should give the only test we yet have of the perfect homogeneity of insulating bodies; for any optical test cannot penetrate, as this does, to the very structure of the molecule.

XXIV. *On the Beats of Consonances of the Form* h : 1.

By R. H. M. Bosanquet.

[Plates VII.–X.]

Ohm's Law, and the Hypothesis of Resultant Displacements.

1. The doctrine known as Ohm's law states that the simplest form of motion by which definite musical pitch is defined to the ear is the pendulum-vibration. It may be extended as follows:—In all cases in which Ohm's law holds, the ear resolves any complex of two or more simultaneous pendulum-vibra-

tions into the original pendulum-vibrations of which they consist, and hears them as distinct and independent sounds.

I rest my belief in Ohm's law mainly on ordinary phenomena, not on refinements or difficult observations; and I shall endeavour to make this my course throughout.

2. So long as, in our mechanical arrangements, we approximate more and more nearly to the condition of things by which we know that simple harmonic vibrations must be produced, we also approximate in the character of the resulting sound to a pure and simple note of definite pitch, free from harmonics and other accompaniments.

So far as simple sounds are concerned, therefore, we receive Ohm's law as being at all events approximately true generally, and in all probability absolutely true when sounds of small intensity alone are considered.

3. When two different sounds are heard together, we have phenomena of which the following is a slight sketch.

If the two sounds are very nearly of the same pitch, they are not heard according to Ohm's law, *i. e.* separately and independently, but in the form of resultant displacements. The most important case is that in which the two sounds are of nearly equal intensity. In this case one sound is heard, intermediate in pitch between the two primaries, and oscillating in intensity between a certain maximum and nothing. These oscillations are what are called the beats of imperfect unisons. Now, as the two notes separate from one another in pitch, the character of the phenomenon changes; and at a certain point the two notes begin to be heard separately and independently, beside the beats which accompany them. It is this phenomenon that is accounted for by Helmholtz's theory of the existence of vibrating bodies, in the ear, having sympathy of a certain definite degree with the various notes.

4. Helmholtz ascertained the approximate degree of this sympathy by considerations of a somewhat indirect character. I wish to point out the important bearing, on the theory, of the direct determination of the interval which separates the region in which two notes are heard only as resultant displacements, from that in which they begin to be heard separately, in accordance with Ohm's law.

5. The experiments I have made on this point have been

mostly conducted by means of my enharmonic organ, in which I have a collection of notes separated for the most part by single commas.

The results, so far as I have gone, are:—1. The critical interval, at which two notes begin to be heard beside their beats, or resultant displacements, is about two commas, throughout that medium portion of the scale which is used in practical music. 2. This critical interval appears not to be exactly the same for all ears. In my own case two notes two commas apart are not heard distinctly beside the beats. In the case of Mr. Parratt, who has kindly examined the point with me, two notes two commas apart are distinctly heard beside the beats. In both cases the beats alone are heard with an interval of one comma, and the two notes are quite clear beside the beats with an interval of three commas.

I propose to undertake further experiments, with the view of determining this initial interval more accurately. So far as the above results go, they are quite consistent with Helmholtz's assumption as to the degree of sympathy of the ear.

6. Independently of any theory, the fact that at a certain point the ear begins to separate out two independent pendulum-vibrations from the resultant displacements, is one that must be recognized. It is easy to show that it is inconsistent with that representation of facts which assumes that beats arise only from the resultant forms exhibited by the superposition of the two vibrations on one receptive mechanism. This is shown as follows.

7. If we combine two vibrations of equal amplitude, which we may take $=1$, $\cos pt$ and $\cos(qt-\epsilon)$, on the same receptive mechanism, the effect is to produce a resultant displacement represented by

$$2\cos\frac{(p+q)t-\epsilon}{2}\cdot\cos\frac{(p-q)t+\epsilon}{2}.$$

This would be heard, by a hypothetical ear receiving the whole disturbance on the same sensorium, as a note whose frequency is the arithmetic mean between the frequencies of the two primaries, and having oscillations of intensity whose frequency is defined by a pendulum-vibration of frequency equal to half the difference of the frequencies of the primaries. This

is what is actually heard in the case of two notes less than two commas apart.

8. When the interval is greater than two commas, this ceases to represent the whole phenomenon perceived by the ear as it exists. The separate notes step in beside the resultant form represented by the above expression, with its beats and note having the frequency of the arithmetic mean. As the interval increases, the separate notes become more and more prominent, and the beats diminish in loudness and distinctness, till, by the time that a certain interval is reached, which is about a minor third in the middle of the scale, the beats practically disappear and the two notes alone survive.

9. It has been supposed by some that the beats disappear only in consequence of their rapidity*; and it is clear that under this supposition, as ordinarily made, lies the assumption that the mass of tone continues to be received in the same manner all the time—*i. e.* that the phenomena of the beats of imperfect consonances and combination-tones are to be explained by reasoning analogous to that of the above formula, which supposes the whole displacement reduced to its resultant on one receptive mechanism. This, for instance, is assumed whenever Smith's or Young's theories of beats are admitted as sufficient explanations of the phenomena.

10. In such cases, (*a*) it is forgotten that the fundamental assumption carries another consequence with it than those it was desired to explain; (*b*) the explanation itself also fails in an important point.

(*a*) The other consequence is, that if it were true that the receptive mechanism of the ear received a resultant displacement, so that the combination was as represented by the above formula, then the primary notes would not be heard at all, and the note that would be heard would have the arithmetic mean of the frequencies of the primaries.

E. g., in the case of a fifth (4 : 6) the note heard would be the major third (5), which would beat very rapidly; just as, when I myself hear the resultant of notes two commas apart, it is one note midway between them beating rapidly. But, as a matter of fact, the note 5 is not heard at all in the above case.

* This is absolutely disproved by the argument in Helmholtz's *Tonempf.* p. 286, ed. 4.

(b) Again, supposing that in some unexplained way the beats whose speed is $\frac{p-q}{2}$ in the above notation gave rise to a note, as supposed by König. Then the speed of that note does not agree with that required for König's first beat-note, which has the same speed as Helmholtz's difference-tone, or $(p-q)$ in the above notation.

11. The relationship of these resultant displacements to the phenomena in the general case, is most conveniently studied by means of the curves drawn by Donkin's harmonograph. The instrument in my possession has a rather restricted number of change-wheels; and one of my first tasks in the St. John's College laboratory has been to cut additional change-wheels for this instrument, for the purpose of illustrating this subject graphically*. (See Plates VII. to X.)

12. The examination of the curves leads us to the following conclusions.

In every case, whether of beats of unisons, or of beats of imperfect consonances, the examination of the curves shows a portion of a harmonic curve lying through the vertices of the single resultant vibrations, which portion corresponds in duration to the beats as given either by Smith's rule or the ordinary rule for beats.

The durations of these harmonic curves are different in different cases. Three principal types may be distinguished:—

Let E, F be the amplitudes; $p : q$ the ratio in lowest terms of the exact consonance whose small variation is considered $(q>p)$.

(1) If E | p is considerably less than F | q, there are q complete harmonic curves both at top and bottom, and the duration of each is q times that of the Smith's beat.

(2) If E | p=F | q, there are $p+q$ complete harmonic curves which may be called external, passing both top and bottom, and the duration of each external curve is $p+q$ times that of the Smith's beat; also there are $q-p$ internal curves, which lie nearer the middle; the duration of each internal curve is $q-p$ times that of the Smith's beat.

(3) If E | p is considerably greater than F | q, there are p

* These curves are of such interest that I devote some space to their discussion, § 77 &c.

harmonic curves both at top and bottom. They are not complete, but appear to form portions of curves of long period.

13. In all cases the curves which correspond to the beats, as ascertained by Smith's method or the ordinary formula, lie like series of bows, one series at the top and the other at the bottom.

The complete period of the pendulum-vibration, of which each of these bows forms a part, is always longer than the single bow or Smith's beat, according to the above rules.

14. Now, according to a well-known principle of mechanics, no pendulum-vibration can give rise to one of another period, in a system in which the forces are proportional to the displacements.

15. In the present case, if we find a term present whose whole period is that of the Smith's beat, it must therefore arise by transformation, *i. e.* through the presence of terms of higher orders than the first. We shall use generally the expression "transformation" to signify the effect on a system of terms higher than the first in the expression for the forces. This is substantially Helmholtz's explanation of the difference-tone, which is identical with the lowest beat-note of König.

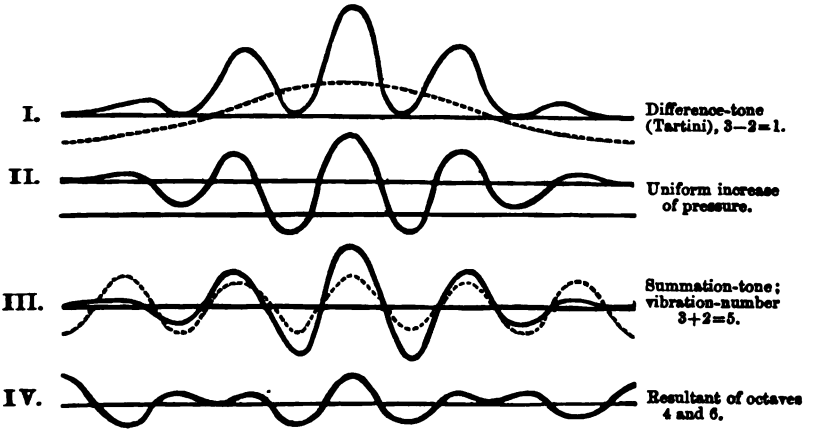
16. We shall show that all König's beat-notes can be accounted for in a similar manner, by the assumption that terms of higher orders become important in the mechanism of the ear when the displacements are considerable.

17. We can illustrate further the difference produced in the curves by the admission of the difference-tone or beat-note as part of the mass of sound. The characteristic difference is, that the medial line is itself bent into a curve, whose whole period is that of the Smith's beat. I have not been able to draw any long curve to show this; but the appearance of the curve at the top of illustration A (p. 227) is very like it in a general way. This illustration represents the square term of the force developed by a fifth (2 : 3) in a transforming system. B is the figure of the total disturbed force in a similar case; but the throwing-up of the medial line is not so prominent as it would be in a longer curve. I have, however, no machine that will draw the combination; and the construction of a long curve of this kind is not worth the labour it would entail.

18. We sum up this part in the following conclusions:—

A.

Statical Analysis of Disturbance proportional to Square of Displacement, showing origin of the combination-tone. Fifth 2 : 3.



I. From disturbance proportional to square of displacement subtract simple e. Amplitude $\frac{1}{2}$ of disturbance. Period = that of the beat. (Vibration-number = difference of vibration-numbers, 3—2=1.)

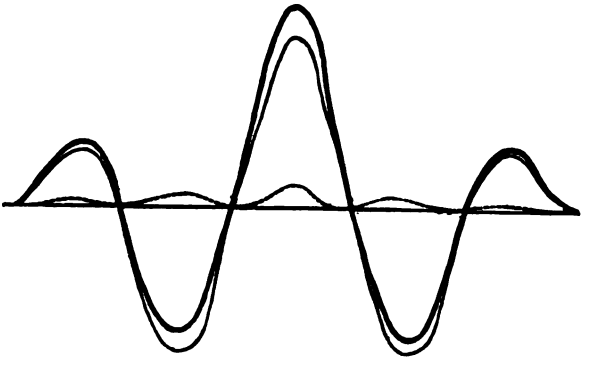
II. Subtract $\frac{1}{2}$ of amplitude of disturbance.

III. Subtract a simple tone. Amplitude $\frac{1}{2}$ of that of disturbance. Period = $\frac{1}{2}$ that of resultant vibration in original beat. (Vibration-number = sum of vibration-numbers of original tones, 3+2=5.)

IV. There remains a succession of beats like the original beats of the fifth, an octave higher, *i. e.* the combination of the octaves of the original notes.

B.

Beat of Fifth, 2 : 3. *Disturbed by term proportional to square of displacement, showing origin of the combination-tone.*



As two notes of equal amplitudes separate from unison, they are at first received by the ear in the manner of resultant displacements, consisting of the beats of a note whose frequency is midway between that of the primaries.

When the interval reaches about two commas, the ear begins to resolve the resultant displacements, and the primary notes step in beside the beats.

When the interval reaches a minor third in the ordinary parts of the scale, neither the beats nor the intermediate pitch of the resultant note are any longer audible, at least as matter of ordinary perception; but the resultant displacement which reaches the ear is decomposed, and produces the sensation of the two primary notes, perfectly distinct from each other: that is to say, Ohm's law has set in, and is true, for ordinary perceptions and in the ordinary regions of the scale, for the minor third and all greater intervals.

19. We may notice here incidentally that it is necessary that the resolved primaries should be uniform and steady, in order that the beats exhibited in the resultant forms may retain their regularity. Those who support the Young-and-Smith theory generally have a sort of confused idea that the primaries are modified when superposed into their resultant.

20. How, then, do the beats of mistuned consonances arise? They may be regarded as springing from interference of new notes, which arise by transformation, in the passage of the resultant forms through the transmitting mechanism of the ear, before the analysis by the sensorium.

Experiments.

21. The engine and bellows* being adjusted to run continuously and quietly, I began to follow the course of König's experiments at the point where he deals with the combinations of the note C, following his form not accurately, but with such divergences as the difference in the apparatus suggested. After going through one or two sets in the way hereinafter described, I concentrated my attention on the analysis of beats, and specially on those of mistuned consonances of the form $h : 1$. It will be seen that after a time I entirely discarded resonators, having convinced myself that, so far as

* See Phil. Mag. Oct. 1880.

they were concerned, the beats of mistuned consonances, other than unisons, with the beat-notes, difference- and combination-tones of all orders, and, in fact, all that I had to observe, were of a purely subjective nature, and were extinguished by resonators properly used, so far as my arrangements enabled me to perceive.

22. The mode in which I then pursued the observations on the beats of the mistuned consonances in question was, to adjust the notes and leave them sounding uniformly and continuously by the hour together. I then walked about the room listening to the combination in all the various forms in which it presented itself, went outside and came in again, always keeping in view the question, what are the sounds that these beats consist of?

23. It is hard to believe that a question to which the answer is tolerably simple could be so difficult. Yet it is *very* difficult; it is one of the most difficult things I ever tried to do, to analyze these apparently complicated sounds into their elements by the ear alone. And when I state my results, I must not be taken to mean that the elements I mention are all that are present. In fact, one of the great difficulties is that there appear to be such a number of different sounds. Some of these are probably due to the imagination; others probably exist in small intensity. And I am satisfied that there still exists a large field of work in the further prosecution of this subject. But of the main result I have no doubt whatever; and that is:—

24. The beats of mistuned consonances of the form $h : 1$, where h is nearly some whole number, consist mainly of variations of intensity of the lower note when the beats of the harmonics are eliminated.

25. I was prepared for this result in the case of the octave by my preliminary experiments (Phil. Mag. viii. p. 293), but did not proceed further till I had verified it and got my ear to perceive it readily under the new conditions, which required two or three days. I then got Mr. Parratt to come and listen. He was much disturbed by the trifling noises from the engine, belts, &c.; and I blew the bellows myself for a time. Eventually he came to the same conclusion, but with an amount of hesitation and difficulty which showed

me what an important element practice is in these observations.

26. I then started these observations with the mistuned twelfth, proceeding in the same way. I seemed to have the same difficulty as before in seizing the phenomenon; and when I eventually decided that these beats were also on the lower note, it was not in pursuance of any preconceived conclusion; for I had no idea at that time of the explanation I now give, and certainly none of the presence of the second difference-tone, or its identity with one of König's beat-notes.

27. Having got so far, I found the remaining verification, of the beats of the mistuned double octave, somewhat easier. These are also on the lower note when they are heard. I have never heard the beats of a mistuned consonance with any wider interval, with the notes I employ, as clear and unmistakable phenomena. Such beats may be discernible by more acute ears, or with notes of a more powerful quality, as they were discerned by König. But in such cases it will be incumbent on the observer to purge the beats from the suspicion of containing the beats of harmonics, as I have done.

28. Mr. Parratt subsequently convinced himself, as before, that the beats of the twelfth and double octave were all heard on the lower notes. I endeavoured, as far as possible, to make his observations independent by avoiding communicating my conclusions to him beforehand.

29. The elimination of the beats of the harmonics depends on the following considerations. The notes employed were examined, with and without resonators, as to the presence of harmonics. These, so far as they are objective, are readily detected with resonators. The beats of the harmonics, where they existed objectively, were also examined with resonators. After a little practice the sound of these beats became familiar enough to prevent their being confused with the beats of the low notes, and the two sets of beats could be observed independently.

30. The only harmonic that exists in these notes in sensible intensity is the twelfth; and this does not appear to originate in the same manner as the principal note. It is heard separately, as it were, and as if it had an independent origin. It

seems probable that it arises in connexion with the movements of the air about the mouth-piece, and not by resonance in the cavity of the bottle, like the principal note. At all events, whatever the cause may be, the effect is that the presence of this note is readily distinguished and allowed for, and there is no risk of its being mixed up with the rest of the phenomenon.

31. The notes employed are of moderate strength. It seems to me that the employment of notes of great power is open to the objection that it introduces all sorts of transformations depending on the greatness of the diplacements; and in this respect alone König's procedure is open to considerable objection. I have confined myself to notes of moderate strength, lying in those regions of the scale which are in ordinary use in music. It is phenomena thus presented that we really seek to understand; and I do not think that any thing is gained by pushing the investigation into those extreme regions where it is possible and highly probable that the ordinary laws of hearing become modified.

32. The first series of notes examined in the above manner were the set of pairs

$$\begin{array}{c} \mathrm{C} : c \\ \mathrm{C} : g \\ \mathrm{C} : c' \\ \hline \mathrm{C} : e' \\ \mathrm{C} : g' \\ \mathrm{C} : c'' \end{array}$$

The beats produced by mistuning, when cleared of the harmonic beats, were heard only in the first three cases.

The second set of pairs was

$$\begin{array}{c} c : c' \\ c : g' \\ \hline c : c'' \\ c : e'' \\ c : g'' \end{array}$$

The beats in question were only heard in the first two cases.

The third set was

$$\begin{array}{c} c' : c'' \\ \hline e' : g'' \\ e' : c''' \end{array}$$

The beats in question were only heard in the first case.

33. In the few experiments hitherto made with notes of higher pitch, the beats of mistuned consonances of the form $h:1$ were not heard when the beats of the harmonics were eliminated, unless the power of the notes was very greatly increased. In this region, however, König's own observations are very full and complete.

34. We notice at once the decrease in the range within which the phenomena are heard as we rise in the scale. This is at once accounted for on the hypothesis of transformation, by the consideration that the displacements to which the higher notes give rise are much smaller than those of the lower notes. If we knew the law of the decrease, we might obtain a relation between the coefficients of the different terms in the expression for the character of the transforming mechanism. König has attempted to formulate a law of decrease; and I have done so on a previous occasion; but this part of the subject is as yet too hypothetical to admit of satisfactory treatment.

Objective and Subjective Phenomena.

Resonators.

35. On beginning work I endeavoured, in the first instance, to ascertain what evidence resonators are capabable of furnishing as to the nature of binary combinations. There are a few points connected with their use which require attention.

36. I have always found difficulty in getting results of a definite character with resonators, whether applied directly to one ear in the manner described by Helmholtz, or connected with one ear by means of a flexible tube, as practised by others. There are three difficulties which occur: (1) pressing the tube or orifice into the ear is apt to close the inner passage of that organ; (2) if the tube or orifice is applied lightly, it does not completely occupy the passage, and external sound comes past it into the ear; and (3) it is impossible so to stop the unused ear as to prevent the external impressions from arriving there and causing confusion.

37. The method I ultimately adopted was as follows:—A copper tube of $\frac{1}{4}$ inch diameter was bent into a semicircle, the diameter of which was nearly 8 inches. At the middle of the tube, and at right angles to its plane, another copper tube was

inserted, 2 inches long, which tapered down to an orifice $\frac{1}{8}$ inch in diameter; this served to communicate with the interior of a resonator by means of a small flexible tube. The extremities of the semicircle were turned inwards and upwards; and into them two brass tubes were inserted, $\frac{3}{4}$ inch long and $\frac{1}{8}$ inch in internal diameter, screwed on the outside. Over each of these was fitted a brass tube, screwed inside, carrying an ivory nipple, such as is used for ear-trumpets. I generally covered the nipple with a couple of thicknesses of thin india-rubber tube.

38. When used, the semicircle is passed under the chin with the resonator-attachment projecting in front. The nipples are at first screwed back as far as possible, brought opposite the orifices of the ears, and then screwed forward until they enter the ears. They are then gradually advanced until the passages are closed to external sounds. Something depends on the way the tube is held. With practice it is possible to hold it so that the passages are closed to external sounds without screwing the nipples in very tight. When they are screwed very tight, it is rather unpleasant, and even painful. But it is necessary constantly to be on one's guard against being deceived by an occasional entrance of external sounds if the nipples are not quite tight. This instrument was made for me some time ago by Mr. Walters of Moorgate Street; it has already been described (Proc. Mus. Assoc. 1879–80, p. 18).

39. The resonators I employ are bottles fitted with corks having apertures of various sizes. I sometimes tune them with water, in the same way as the bottle-notes; sometimes I insert tubes into the apertures to lower the pitch. A bit of small glass tubing passed through the cork is connected by an india-rubber tube with the above-described ear-piece.

40. By means of these arrangements I some time ago examined the nature of the ordinary first difference-tone, and convinced myself that it is not capable of exciting a resonator (*l. c.* p. 20). This conclusion has also been arrived at by others*. In short, the difference-tone of Helmholtz, or first beat-note of König, as ordinarily heard, is not objective in its character. It is therefore subjective. (See Helmholtz, *Ton-*

* Preyer, *Akustische Untersuchungen*, p. 13.

empfindungen, 4th ed. p. 259.) In making the experiment of listening for the difference-tone through a resonator, it is necessary to be careful that the ears are both closed to external sounds; otherwise the external notes will penetrate through, the difference-tone will appear, and the completeness of the cut-off effected by the resonator will be entirely lost.

41. When beginning the regular course of experiments according to the general outline of König's work, I was careful, in the first instance, to examine the various masses of sound presented, with resonators arranged as above indicated. In examining, for instance, the intervals made by the note C with the various notes of the octave above it (up to *c*), I first fixed the resonator at some one pitch, and then ran the movable note up through the octave. Then, as this did not seem a good process for analysis, I set the mistuned octave beating, or any other combination it was desired to examine, and ran the pitch of the resonator up and down with water to see if any thing could be detected. And here I came across an observation that puzzled me for some time.

42. Suppose the mistuned octave C : *c* was sounding, and I examined the lower note with the resonator: sometimes it appeared loud and steady, at other times as if beating powerfully. On removing the resonator-attachment from the ear, the lower note was always heard to beat powerfully. The explanation was simple. When the nipples of the resonator-attachment fitted tightly into the ears, nothing reached the ear but the uniform vibrations of the resonator sounding C. But if there was the slightest looseness between the nipple and the passage of either ear, the second note (*c*) of the combination got in, and gave rise to the subjective difference-tone (first beat-note of König), by interference of which with the C I explain the beats on that note. *These beats are therefore subjective.*

43. A considerable number of combinations, including examples of the principal forms of beat, rattle, or roll, were examined in this way; and when the precautions above indicated were attended to, the results were in all cases to negative the objective existence of all forms of beats, and beat-notes or difference-tones, except the beats which arise from the interference of approximate unisons, which beats arise from

both notes acting on the resonator simultaneously. This of course includes the beats produced by objective harmonics.

Course of General Experiments.

44. The following is the detailed examination of the combinations of the note C, made in a continuous and connected manner. The results have a general correspondence with those of König. The numerous rattles and rolls of beats mentioned were not further analyzed for the most part: the analysis of these is very difficult; and, as has been already stated, a separate investigation is required in every such case. Some attention was devoted to beats of the mistuned fifth, both in the case mentioned and in others; but no final result was arrived at. In two different cases of mistuned fifths (2 : 3, nearly), I had a strong impression that the note 7 formed an important part of the beat. This would be a summation-tone of the second order, thus $2 \times 2 + 3$. I am confident that it did not arise from harmonics.

These experiments were made after some experience had been gained.

C : C.

Rattle up to

C : F.

Slow beats up to

C : G, smooth fifth. Roll only perceptible when the ear is held close to the two sources of sound.

——, 5 beats sharp. Perception of pitch very difficult in this part of the scale. There is a heavy beat like a knock, which appears to affect the whole mass of sound*. The low beat of C_1 is only distinguishable with difficulty, or hardly at all.

(Another occasion.) Mr. Parratt describes the fifth C : G, beating slowly, as consisting of E♭ and C_1 in addition to the primary notes; the mass of the beat is at least partly on E♭. I do not hear the E♭, but seem to hear the note E.

(Another occasion.) Mr. Parratt is clear that the beat of the mistuned fifth C : G is on C_1 alone; but he still

* I take this entry to show that no progress had been made with the resolution of the phenomenon into its elements.

hears the E♭ in the mass of tone. I seem to hear the beats both on C and C_1; but I have a difficulty in separating the octaves in this deep pitch.

C : G, 8 beats sharp. Clear rattle, with suspicion of roll beside it.

—— 10 beats sharp. Beats just distinguishable. Roll.

C : B♭. Rattle emerges.

Below

C : *c*, 8 beats can be counted.

——, 4 beats very distinct. Consist entirely of variation of intensity of lower note. This effect is very clear and remarkable.

——, a very slow beat flat. Here it was easy to recognize the effect of the shift of phase in the apparent great increase of volume of the lower note at one period of the change. The upper note was not perceptibly affected.

C : *c*. A slight rich roll with smooth tone. The production of the roll depends a good deal on the phase, as is seen by leading up to *c* with a very slow beat.

The twelfth of the C was plainly distinguishable, but it appeared to keep separate from the mass of tone; it was perfectly steady and unaffected by combination with *c*.

C : *c*, 2 beats sharp. Phenomena undistinguishable from 2 beats below.

——, 4 beats sharp. Perhaps a little less roll in the strong part of the beat.

——, 8 beats sharp. The mass of the beats is of pitch near C; but the exact pitch is very difficult to distinguish. It is a deep heavy rattle, quite distinct in pitch from the upper note.

C : *e*. If there is any slow beat in passing through this, it is very difficult to distinguish. I am inclined to negative it.

C : *f*♯. Roll.

Slow beats up to

C : *g*. These beats consist of alternations of intensity of C. They are more difficult to count than those of C : *c*. I counted them at 5 below.

——. Slow beats above.

C : *b*♭. Rattle, turning into beats easily counted at 4 below

c'. These beats also consist of variations of intensity of the lower note.

C : c'.

The beats above c' were also counted at 4 above, while the engine was going, without difficulty.

45. Above this, in the neighbourhood of the binary consonances C : c' &c., I have never been able to obtain slow beats in such a way that they could be readily perceived (even without the engine) or certainly counted.

46. The mode adopted to examine cases in which the beats could not be perceived was, to introduce a third note, such as c', which gave beats with the C, and tune it true. Then any note, such as e' or g', could be readily tuned so that the whole three notes gave 1, 2, 3, or 4 beats. When this had been done, the intermediate note c' was removed. If the pair examined was capable of giving beats at all, they should then have been audible.

47. The details of the above course furnish no new results; I have not, therefore, thought it worth while to give similar courses for other sets of notes. Those results which are worthy of mention have been already stated.

Theory of the Beats of Mistuned Consonances of the form h : 1.

48. Let n be the frequency of the lowest note, m the number of beats per second. Then the mistuned octave is $n : 2n \pm m$; the mistuned twelfth is $n : 3n \pm m$; and so on.

49. Beats of the mistuned octave,

$$n : 2n \pm m.$$

Number of beats $= m$.

m variations of intensity of the lower note (n) are produced by interference of notes n and $n \pm m$; and $n \pm m$ is the first combination-tone (difference-tone of form $p - q$), of the primaries n and $2n \pm m$.

This rests chiefly on the observation that the beats, when the octave harmonic is eliminated, consist entirely of variations of intensity of the lower note.

The existence of the first combination-tone in question ($p - q$) is well known. It is easily demonstrated in the neighbouring case of intervals not far removed from the fifth, when

the beats of the first two combination-tones are specially prominent (secondary beats of König).

50. Beats of the mistuned twelfth,

$$n : 3n \pm m,$$

Number of beats $= m$.

m variations of intensity of the lower note (n) are produced by interference of notes n and $n \pm m$. And $n \pm m$ is the second combination-tone (difference-tone of form $2p - q$) of the primaries n and $3n \pm m$.

This rests also chiefly on the observation that the beats, when the third partials are eliminated, consist entirely of variations of intensity of the lower note.

The existence of the second combination-tone in question ($2p - q$) is demonstrated in many cases by König. It is easily heard in the case of intervals near the octave high in the scale. It is also easily detected by the secondary beats which it forms with the first combination-tone in the case of intervals near the fifth—also less easily by the secondary beats which it forms with the third combination-tone in intervals near 2 : 5, at which point the second and third combination-tones coincide.

51. Beats of the mistuned fifteenth or double octave,

$$n : 4n \pm m.$$

Number of beats $= m$.

m variations of intensity of the lower note (n) are produced by interference of notes n and $n \pm m$. And $n \pm m$ is the third combination-tone (difference-tone of form $3p - q$) of the primaries n and $4n \pm m$.

This rests also chiefly on the observation that the beats, when the fourth partials are eliminated, consist entirely of variations of intensity of the lower note.

The existence of the third combination-tone in question ($3p - q$) is demonstrated in many cases by König. It is heard not so easily as the lower combination-tones, in the case of intervals near the twelfth high in the scale. It is also less easily detected by the secondary beats which it forms with the second combination-tone in the case of intervals near 2 : 5, at which point the second and third combination-tones coincide—also much less easily by the secondary beats which it forms with the fourth combination-tone in the case of inter-

vals near 2 : 7, at which point the third and fourth combination-tones coincide.

52. Beats of the mistuned tierce (two octaves and a major third), $n : 5n \pm m$.

These beats are much less easily detected in pure notes of the ordinary strength than any of the foregoing. They are recorded by König; but I have never heard them clearly. As it is certain that König's notes were not perfectly pure, and he does not analyze the beats, we cannot tell whether the variations of the lower note were produced in his experiments. If they were, they are to be accounted for in a similar manner.

Number of beats $= m$.

m variations of intensity of lower note (n) are produced by interference of notes n and $n \pm m$. And $n \pm m$ is the fourth combination-tone (difference-tone of form $4p - q$) of the primaries n and $5n \pm m$.

The existence of the fourth combination-tone in question ($4p - q$) is demonstrated directly by König in the case of intervals near the double octave $c''' : c^{v}$. It is also less easily detected by the secondary beats which it forms with the third combination-tone in the case of intervals near 2 : 7, at which point the third and fourth combination-tones coincide.

53. Beats of the mistuned consonance of the nineteenth are recorded by König;

$$n : 6n \pm m.$$

Number of beats $= m$.

m variations of intensity of lower note (n) might be produced by interference of n and $n \pm m$. And $n \pm m$ is the fifth combination-tone (difference-tone of form $5p - q$) of the primaries n and $6n \pm m$.

The existence of the fifth combination-tone in question ($5p - q$) is not anywhere directly demonstrated. Secondary beats, which might be produced by its interference with the fourth combination-tone, are recorded by König in the neighbourhood of the interval $c : d''$

54. Beats of the mistuned consonance 1 : 7 are recorded by König. These might be produced by a sixth combination-tone (difference-tone of form $6p - q$) of the primaries n and $7n \pm m$.

55. Beats of the mistuned consonance 1 : 8 are recorded. These might be produced by a seventh combination-tone (difference-tone of form $7p-q$) of the primaries $8n \pm m$.

56. As far as my own experience goes, however, I have no direct and palpable evidence of beats of mistuned consonances higher than 1 : 4, or of the existence of combination-tones higher than the third ($3p-q$) in recognizable intensity. Up to this point the phenomena are quite clear; and there is no possible doubt as to their nature.

But in considering these limited results it must be remembered, (1) that I have restricted myself to notes of very moderate intensity, so that the phenomena might correspond as nearly as possible to those which are presented to our ears in practice, and (2) that, although I was unable to get rid entirely of the presence of upper partials in all cases, yet the phenomena were subjected to a careful and prolonged analysis by listening under varied conditions, until the effect of the upper partials could be separated out and eliminated with certainty. And we have at all events no security that these upper partials did not give rise to many of König's results; indeed it is almost certain that they must have entered into those results.

Note.—The present paper was written before the appearance of König's paper in Wiedemann's *Annalen* in the present year. The discussion of that paper, though necessary for a complete view of the subject, must be reserved till after the conclusion of the present paper.

Combination-Tones arising from Terms of Orders higher than the first, in the Transforming-structure of the Ear.

57. Helmholtz pointed out the way in which the hypothesis of asymmetry in the transmitting mechanism of the ear gives rise to the combination-tone of the first order, which he called the difference-tone. This asymmetry was represented in his investigation by a term of the second order in the force called into play by a given displacement. Helmholtz further indicated the tones to which the existence of terms of the third order gives rise, and pointed out that tones of the fourth order &c. would give rise to other combination-tones not further specified.

58. In specifying those combination-tones which arise from

the terms of the third order, Helmholtz pointed out that one of them was a combination-tone of the second order "in the sense indicated by Hallström." This is also the sense in which the expression "combination-tone of the second order" is used by Helmholtz himself in the text of his work; and it means apparently a combination-tone which arises from a combination-tone or combination-tones of the first order when combined with any other notes present, or with each other, according to the law of combination-tones of the first order.

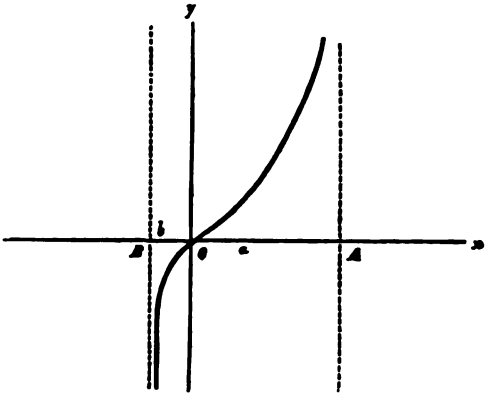
59. It is clear, however, that the principal combination-tones which arise from the terms of higher orders in the transmitting mechanism of the ear, are derived directly from the primary tones, and are not materially influenced by the secondary series of tones. This is obvious, on the one hand, since all the resultant tones, according to the principles of their origin, are of the nature of small quantities compared with the primary tones, and, on the other hand, because the tones derived from the terms of higher orders are in fact produced with the greatest intensity when the tones derived from terms of lower orders are weak or evanescent. This fact has been used by König as one of the most powerful objections to the theory of combination-tones as hitherto expounded; and, indeed, the objectionable character of some of the hypothetical derivations by combination given by Helmholtz* must have struck many readers independently.

60. I shall now examine Helmholtz's hypothesis of asymmetry in a little more detail; and I think it will appear that it leads, by tolerably simple mathematical treatment, to the development of the combination-tones of the higher orders, under the circumstances under which they actually exist, and independently of the combination-tones of the lower orders.

61. Let 0 represent the position of rest of a point free to move along the line $0x$ between the points A and B, subject to certain forces in that line. Suppose that these forces are of the nature of springs tending to resist the departure from 0, and that on arrival at the points A, B, at distances a, b, from 0 on either side, the springs ultimately go up against dead walls, so that further displacement is resisted with an infinite

* *Tonempfindungen*, 4th ed. p. 329; also p. 327, where the combinations are supposed to be formed with the partials of the primaries as well.

force. If we set off the forces as ordinates, they may be represented as in the figure; and analytically they may be ex-



pressed by such an assumption as

$$y=\frac{kx}{\left(1-\frac{x}{a}\right)\left(1+\frac{x}{b}\right)}$$

Expanding this function in a series proceeding by powers of x, we have an example of a law of force expressed by such a series, which for small displacements coincides with the pendulum law, while for displacements of but moderate extent the higher terms rapidly become prominent.

62. Assuming the existence of a law of this kind in the transmitting mechanism of the ear, we should have for the force corresponding to displacement u such an expression as

$$-(n^2u+\alpha u^2+\beta u^3+\gamma u^4+\dots).$$

Suppose the system acted upon by two harmonic forces,

$$\mathrm{E}\cos pt,\quad \mathrm{F}\cos(qt-\epsilon),$$

and the mass = unity, or included in the coefficients; the equation of motion is

$$\frac{d^2u}{dt^2}+n^2u=-\alpha u^2-\beta u^3-\gamma u^4\dots+\mathrm{E}\cos pt\,\mathrm{F}\cos(qt-\epsilon)$$

(following the notation of Lord Rayleigh on Sound, i. p. 65).

For the first approximation we neglect powers of u above

the first; then

$$u = e\cos pt + f\cos(qt-\epsilon),$$

where

$$e = \frac{E}{n^2-p^2}, \quad f = \frac{F}{n^2-q^2}.$$

63. We may here mention that, in the present case, n is negligible. This is easily seen, since, if n had any value corresponding to a frequency within the limits of the ordinary range of hearing, there would be a series of notes strengthened by the correspondence. But the only notes thus strengthened are those which are supposed to correspond to the ear-cavity. They are so high in the scale that the connexions of the internal ear would require to be nearly as rigid as brass or steel to produce them. A further reason for n not being large will be arrived at in speaking of combination-tones. And we shall assume that n is smaller than any values of p or q which occur in practice.

64. The first approximations to the subsequent terms may be now all made by substituting in them the value of u above obtained. The process to be followed for u^2 coincides with that commonly adopted; and the result is given in Lord Rayleigh's book, i. p. 66.

In the cases of u^3 and higher powers the process is simpler than that which has been previously indicated.

65. In virtue, however, of the preceding considerations concerning the value of n, we may materially simplify the whole process for our present purpose by neglecting the term n^2u altogether. The original equation then assumes the form

$$\frac{d^2u}{dt^2} = -(\alpha u^2 + \beta u^3 + \ldots) + E\cos pt + F\cos(qt-\epsilon).$$

First approximation,

$$\begin{aligned} u &= D^{-2}\left(E\cos pt + F\cos(qt-\epsilon)\right) \\ &= -\left(\frac{E}{p^2}\cos pt + \frac{F}{q^2}\cos(qt-\epsilon)\right) \\ &= -\left(e\cos pt + f\cos(qt-\epsilon)\right) \text{ say.} \end{aligned}$$

Substituting this in the remaining terms, we get

$$\frac{d^2u}{dt^2} = \mathrm{E}\cos pt + \mathrm{F}\cos(qt-\epsilon)$$
$$-\alpha\left(e^2\cos^2 pt + f^2\cos^2(qt-\epsilon) + 2ef\cos pt\cos(qt-\epsilon)\right)$$
$$-\beta\left(e^3\cos pt + f^3\cos^3(qt-\epsilon) + 3e^2f\cos^2 pt\cos(qt-\epsilon) + 3ef^2\cos pt\cos^2(qt-\epsilon)\right)$$
$$-\gamma\left(e^4\cos^4 pt + f^4\cos^4(qt-\epsilon) + 4e^3f\cos^3 pt\cos(qt-\epsilon) + 6e^2f^2\cos^2 pt\cos(qt-\epsilon) + 4ef^3\cos pt\cos(qt-\epsilon)^3\right)$$
$$- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad ;$$

and u is, to this first approximation with respect to all terms, the integral taken twice with respect to t of the right-hand side of the above equation.

66. There is, no doubt, a difficulty as to the absolute neglect of the term n^2u. The effect is to make the vibrating-point apparently rest in a position which is not one of equilibrium. Nevertheless the application of the facts to Helmholtz's hypothesis requires this proceeding; and it makes no difference whether it is done finally or at first. I think it very probable that damping terms, depending on the second and higher powers of the velocity, play an important part in the real explanation. The source of the terms, however, is of secondary importance in the present state of the question. The point is to show that those resultant sounds which depend on terms of higher orders can become great independently of those which depend on terms of lower orders.

67. Collecting the terms up to the fourth order, transforming them into multiple arcs, and writing $pt=\theta$, $qt-\epsilon=\phi$, the equation becomes

$$\frac{d^2u}{dt^2} = \mathrm{E}\cos\theta + \mathrm{F}\cos\phi$$
$$-\left[\frac{\alpha}{2}(e^2+f^2) + \frac{3}{8}\gamma(e^4+f^4+4e^2f^2)\right.$$
$$+\tfrac{3}{4}\beta\{(e^2+2f^2)e\cos\theta + (2e^2+f^2)f\cos\phi\}$$
$$+\frac{e^2}{2}\{\alpha+\gamma(e^2+3f^2)\}\cos 2\theta + \frac{f^2}{2}\{\alpha+\gamma(3e^2+f^2)\}\cos 2\phi$$
$$\left.+\frac{\beta}{4}(e^3\cos 3\theta + f^3\cos 3\phi)\right.$$

$$+\frac{\gamma}{8}(e^4\cos 4\theta+f^4\cos 4\phi)$$

$$+ef\{\alpha+\tfrac{3}{2}\gamma(e^2+f^2)\}(\cos(\theta+\phi)+\cos(\theta-\phi))$$

$$+\tfrac{3}{4}\beta e^2 f\{\cos(2\theta+\phi)+\cos(2\theta-\phi)\}$$

$$+\tfrac{3}{4}\beta ef^2\{\cos(\theta+2\phi)+\cos(\theta-2\phi)\}$$

$$+\tfrac{3}{4}\gamma e^2f^2\{\cos 2(\theta+\phi)+\cos 2(\theta-\phi)\}$$

$$+\gamma\frac{e^3f}{2}\{\cos(3\theta+\phi)+\cos(3\theta-\phi)\}$$

$$+\gamma\frac{ef^3}{2}\{\cos(\theta+3\phi)+\cos(\theta-3\phi)\}\Big].$$

68. On performing the double integration, we shall find the constant term in the above multiplied by t^2, an inadmissible result. It is only necessary to look back to the result of the complete process, when we find that the term in question is represented after integration by $\frac{\text{constant}}{n^2}$, where n^2 is the small coefficient of the term we have neglected. This indicates that the position of equilibrium is indeed displaced, but through a finite amount; as this does not affect our results, we omit the term in question.

69. Remembering that $\theta=pt$ and $\phi=qt-e$,

$$e=\frac{\mathrm{E}}{p^2},\quad f=\frac{\mathrm{F}}{q^2},$$

the remainder of the equation becomes

$$u=-e\cos\theta-f\cos\phi$$

$$+\tfrac{3}{4}\beta\left\{\frac{e^2+2f^2}{p^2}e\cos\theta+\frac{2e^2+f^2}{q^2}f\cos\phi\right\}$$

$$+\frac{e^2}{2}\frac{\alpha+\gamma(e^2+3f^2)}{4p^2}\cos 2\theta+\frac{f^2}{2}\frac{\alpha+\gamma(3e^2+f^2)}{4q^2}\cos 2\phi$$

$$+\frac{\beta}{4}\left(\frac{e^3}{9p^2}\cos 3\theta+\frac{f^3}{9q^2}\cos 3\phi\right)$$

$$+\frac{\gamma}{8}\left(\frac{e^4}{16p^2}\cos 4\theta+\frac{f^4}{16q^2}\cos 4\phi\right)$$

$$+ef\{\alpha+\tfrac{3}{2}\gamma(e^2+f^2)\}\left(\frac{\cos(\theta+\phi)}{(p+q)^2}+\frac{\cos(\theta-\phi)}{(p-q)^2}\right)$$

$$+\tfrac{3}{4}\beta e^2 f\left\{\frac{\cos(2\theta+\phi)}{(2p+q)^2}+\frac{\cos(2\theta-\phi)}{(2p-q)^2}\right\}$$

$$+\tfrac{3}{4}\beta e f^2\left\{\frac{\cos(\theta+2\phi)}{(p+2q)^2}+\frac{\cos(\theta-2\phi)}{(p-2q)^2}\right\}$$

$$+\tfrac{3}{4}\gamma e^2 f^2\left\{\frac{\cos 2(\theta+\phi)}{4(p+q)^2}+\frac{\cos 2(\theta-\phi)}{4(p-q)^2}\right\}$$

$$+\gamma\frac{e^3 f}{2}\left\{\frac{\cos(3\theta+\phi)}{(3p+q)^2}+\frac{\cos(3\theta-\phi)}{(3p-q)^2}\right\}$$

$$+\gamma\frac{e f^3}{2}\left\{\frac{\cos(\theta+3\phi)}{(p+3q)^2}+\frac{\cos(\theta-3\phi)}{(p-3q)^2}\right\};$$

so that there are six summation-tones and six difference-tones produced by direct transformation of the primaries, when the effect of terms up to the fourth order is considered.

70. The effect of the neglect of n^2 in the denominators of all these terms, is to place the principal development of any term such as the difference-tone $p-q$ at the point where $p-q=0$, whereas if the complete solution were retained the condition for the principal development would be

$$n^2-(p-q)^2=0.$$

No known phenomenon enables us to distinguish between these two cases. Every thing happens, so far as we know, precisely as if the simpler condition were that which is really important.

71. If we proceed to terms of higher orders in the same way, we shall always have, in the result of terms of the $\overline{n+1}$th order, the two following terms representing nth difference-tones, which alone are important for our present purpose (α_{n+1} is the $\overline{n+1}$th coefficient),

$$\frac{(n+1)\alpha^{n+1}}{2^n}\left\{\frac{e^n f\cos(n\theta-\phi)}{(np-q)^2}+\frac{e f^n\cos(\theta-n\phi)}{(p-nq)^2}\right\},$$

besides other terms analogous to those shown above.

72. In the neighbourhood of any consonance of the form $h:1$, the terms having the denominators $(hp-q)^2$ become large; this is Helmholtz's explanation of the origin of difference-tones, generalized.

73. As the argument from the analytical expressions fails to give perfect satisfaction unless the nature of the causes

involved be more directly demonstrated, I shall try to show more simply how it is that this comes about.

In periodic functions such as $\cos pt$, $\cos(qt-\epsilon)$, the quantities p, q are such that, if τ, τ' be the periodic times,

$$p\tau = q\tau' = 2\pi, \text{ or } p = \frac{2\pi}{\tau}, \quad q = \frac{2\pi}{\tau'}.$$

If, then,

$$\mathrm{M}\tau = 1,$$
$$\mathrm{N}\tau' = 1,$$

M, N are the frequencies of the primaries, and

$$p = 2\pi\mathrm{M}, \quad q = 2\pi\mathrm{N}.$$

In the case of a mistuned consonance of the form $h:1$, the denominator of the h difference-tone term in the above expression will be $4\pi^2(h\mathrm{M}-\mathrm{N})^2$. And $h\mathrm{M}-\mathrm{N}$ is the frequency of the beat which gives rise to the transformation according to all theories (putting $k=1$ in the more general formula $h\mathrm{M}-k\mathrm{N}$).

$\therefore \frac{1}{h\mathrm{M}-\mathrm{N}}$ is the time of duration of the beat of the resultant form, whether we call it the Smith's beat, or the bow of the pendulum curves. As the denominator diminishes, the time or duration of the beat increases.

74. What happens, then, is that a force is developed, by the influence of the higher terms in question, which acts for a time corresponding to the duration of the beat. And it is matter of ordinary mechanical knowledge that, under these circumstances, the space traversed is proportional to the square of the time during which the action lasts; so that when the beat is lengthened the effect of the transformation is strengthened.

75. It is possible to found an independent treatment of the subject on these considerations, the course of which would be somewhat as follows.

In mistuned consonances of the form $h:1$ there are alternate increases and diminutions of the maximum resultant displacement, the duration of which can be arrived at by the considerations employed by Smith in determining the duration of beats. The duration of one such increase and diminution can be shown by the known formula to be $\frac{1}{h\mathrm{M}-\mathrm{N}}$.

Assume that the transmitting mechanism of the ear possesses such powers of transformation that any regular sequence of increases and diminutions of maximum resultant displacement is capable of giving rise, by transformation, to a subjective note having the same period as that of one increase and diminution. This assumption only differs from that made above in definiteness of form; for the algebraic series which is above proved to give rise to transformations of this description, is itself an assumption.

It immediately follows, by considerations differing little from those made use of in the ordinary investigation of the motion of a particle under the action of a uniform force, that the coefficient of the term in question will contain the square of the periodic time—that is to say, the coefficient $\frac{1}{(hM-N)^2}$; and this is the essential point proved by the more complete analytical investigation above given.

76. Though perhaps defective as a complete demonstration of the *rationale* of the origin of difference-tones, these considerations render the general meaning of the coefficients of the difference-tone terms in the above equations tolerably clear. And we have thus sketched a method, in which the doctrine of transformation arising out of the Smith's beats, as the resultant forms pass through the transmitting mechanism of the ear, forms the basis for the further explanation of the phenomena of beats as we find them.

The Resultant Wave-forms of Mistuned Consonances.

77. I am principally acquainted with these forms as drawn by means of Donkin's harmonograph. The curves (Plates IV.–VII.) that accompany this paper exhibit all the points on which it will be necessary to touch.

78. It is hardly possible to be acquainted with these curves without seeing that the figures formed by the vertices which occur in the curves are in some way related to the phenomena of the mistuned consonances. And as I had myself considerable difficulty in coming to definite conclusions as to the real nature of this relation, and do not know of any published discussion of the subject, I add this article dealing with the relation in question so far as it is connected with the subject of the paper.

79. The curves are referred to an axis of x, along which the wave-lengths are measured, and an axis of y parallel to which the displacements are measured. λ and λ' are the wave-lengths on the paper of the two primary curves. If it is required to consider a question of frequency, the paper must be supposed to be drawn past the observer with velocity v, when the frequencies will be $\frac{v}{\lambda}, \frac{v}{\lambda'}$ respectively.

80. The tangent of the inclination of a curve to the x-axis will be spoken of shortly as the "slope."

It is assumed that $q\lambda' = p\lambda + \delta$, where p, q are integers, $q > p$, and δ is small.

81. The equation of the resultant of two primary curves may then be written

$$y = \mathrm{E}\cos 2\pi\frac{x}{\lambda} + \mathrm{F}\cos\frac{2\pi}{\lambda'}(x-\alpha).$$

The slopes of the two single curves are

$$-\frac{2\pi}{\lambda}\mathrm{E}\sin 2\pi\frac{x}{\lambda}, \quad -\frac{2\pi}{\lambda'}\mathrm{F}\sin\frac{2\pi}{\lambda'}(x-\alpha).$$

The ratio of the coefficients is

$$\frac{\lambda'\mathrm{E}}{\lambda\mathrm{F}} = \frac{p\mathrm{E}}{q\mathrm{F}} \text{ nearly.}$$

When this ratio is much greater than unity, the resultant slope is nearly that of the first term. When it is much less than unity, the resultant slope is nearly that of the last term.

82. The general expression for the resultant slope is given by

$$\frac{dy}{dx} = -\frac{2\pi}{\lambda}\mathrm{E}\sin 2\pi\frac{x}{\lambda} - \frac{2\pi}{\lambda'}\mathrm{F}\sin\frac{2\pi}{\lambda'}(x-\alpha).$$

The vertices of the resultant curve are obtained by equating $\frac{dy}{dx}$ to zero, whence

$$\frac{\mathrm{E}}{\lambda}\sin\frac{2\pi x}{\lambda} + \frac{\mathrm{F}}{\lambda'}\sin\frac{2\pi}{\lambda'}(x-\alpha) = 0.$$

83. Case I., where F is great, and the first term negligible compared with the second ($\frac{\lambda'\mathrm{E}}{\lambda\mathrm{F}}$ small).

Here the vertices are those of the second component of the curve. Consequently, in every cycle of p and q vibrations of

λ and λ' respectively, the q vertices of λ' appear, those of λ being smoothed out. The sole effect of the term involving λ is in this case to modify slightly the positions of the vertices.

84. If, then, $p\lambda$ were exactly $=q\lambda'$, then after a certain distance, which may be called a short cycle, the vertices would recur for precisely the same values of y. And the corresponding vertices in successive short cycles would lie on q straight lines, or on $2q$ straight lines if the lower vertices be included.

This short cycle is obviously $p\lambda=q\lambda'$ in duration.

85. Since, however, in our general case $p\lambda+\delta=q\lambda'$, the coincidence after the short cycle is not exact; but the vertex determined by equating the second term of the inclination to zero has, in the first term, a different correction to the value of y from that which existed before the short cycle.

86. At the vertex before the short cycle let $x=\alpha$, so that the second term of the inclination vanishes; then, before the short cycle,

$$y_0=\mathrm{E}\cos\frac{2\pi\alpha}{\lambda}+\mathrm{F};$$

after one short cycle, $x=q\lambda'+\alpha=p\lambda+\delta+\alpha$,

$$y_1=\mathrm{E}\cos\frac{2\pi}{\lambda}(\alpha+\delta)+\mathrm{F};$$

after two short cycles, $w=2q\lambda'+\alpha=2(p\lambda+\delta)+\alpha$,

$$y_2=\mathrm{E}\cos\frac{2\pi}{\lambda}(\alpha+2\delta)+\mathrm{F};$$

and so on, till after n short cycles, where $n\delta=\lambda$, nearly or exactly,

$$y_n=\mathrm{E}\cos\frac{2\pi\alpha}{\lambda}+\mathrm{F};$$

and the ordinate of the vertex in question has gone through a complete period of a pendulum-curve in the space

$$\begin{aligned} nq\lambda' &= n(p\lambda+\delta) \\ &= n\lambda\left(p+\frac{1}{n}\right), \text{ since } n\delta=\lambda \\ &= \lambda(np+1). \end{aligned}$$

87. Now we have seen that there are q of these vertices, each of which gives rise to one of these curves. Consequently

this space, $(np+1)\lambda = nq\lambda'$, presents, both above and below, q projecting bows, and each bow is of length

$$\frac{np+1}{q}\lambda \text{ or } n\lambda'.$$

This is the length of Smith's beat, or of the beat as given by a well-known formula. This is easily verified as follows:—

88. Let v be the velocity of sound corresponding to wave-lengths λ and λ', and M, N the corresponding frequencies; then

$$\frac{v}{\lambda} = \mathrm{M}, \quad \frac{v}{\lambda'} = \mathrm{N},$$

and $q\lambda' = p\lambda + \delta$ becomes $(n\delta = \lambda)$,

$$\frac{q}{\mathrm{N}} = \frac{p}{\mathrm{M}} + \frac{1}{n\mathrm{M}};$$

$$\therefore p\mathrm{N} - q\mathrm{M} = \frac{\mathrm{N}}{n} = \frac{v}{n\lambda'};$$

which connects the expression above obtained with the ordinary formula for the frequency of the beat. Hence the Smith's beat in this case corresponds in period to the projecting bow formed by the $\frac{1}{q}$th part of the whole periodic curve of slow disturbance of one of the vertices.

89. Case II., where $\frac{\mathrm{E}}{\lambda} = \frac{\mathrm{F}}{\lambda'}$, so that the condition for a vertex reduces to

$$\sin\frac{2\pi x}{\lambda} + \sin\frac{2\pi}{\lambda'}(x-\alpha) = 0.$$

This condition gives the following series of values:—

$$\begin{aligned} \frac{x}{\lambda} &= \frac{-x+\alpha}{\lambda'}, & x &= \frac{\alpha\lambda}{\lambda+\lambda'}, \\ &= \frac{-x+\lambda'+\alpha}{\lambda'}, & &= \frac{(\alpha+\lambda')\lambda}{\lambda+\lambda'}, \\ &\cdots\cdots & &\cdots\cdots \\ &= \frac{-x+\nu\lambda'+\alpha}{\lambda'}, & &= \frac{(\alpha+\nu\lambda')\lambda}{\lambda+\lambda'}, \end{aligned}$$

until

$$\nu\lambda' = \lambda + \lambda';$$

and if

$$q\lambda' = p\lambda,$$

$$\nu = \frac{p+q}{p}.$$

Where this is not a whole number, the condition will be

$$\nu\lambda' = k(\lambda+\lambda'),$$

$$\nu = k.\frac{p+q}{p};$$

and if $p : q$ is in its lowest terms,

$$k = p, \text{ and } \nu = p+q,$$

$p+q$ is therefore the number of independent vertices arising from these terms.

90. Another series of values satisfies the condition; these are as follows (since $\sin x = \sin(\pi - x)$ &c.):—

$$\frac{x}{\lambda} = \frac{1}{2} + \frac{x-\alpha}{\lambda'}, \qquad x = \frac{\lambda'-2\alpha}{2(\lambda'-\lambda)}.\lambda,$$

$$= \frac{3}{2} + \frac{x-\alpha}{\lambda'}, \qquad = \frac{3\lambda'-2\alpha}{2(\lambda'-\lambda)}.\lambda,$$

. . . .

$$= \frac{2\nu-1}{2} + \frac{x-\alpha}{\lambda'}, \qquad = \frac{(2\nu-1)\lambda'-2\alpha}{2(\lambda'-\lambda)}.\lambda,$$

until

$$(2\nu)\lambda' = 2(\lambda-\lambda'),$$

$$\nu = \frac{\lambda'-\lambda}{\lambda'},$$

$$= \frac{p-q}{p}.$$

And if this be not a whole number,

$$(2\nu)\lambda' = 2k(\lambda-\lambda'),$$

$$\nu = k\left(\frac{q}{p}-1\right),$$

$$\nu = \frac{k}{p}(p-q);$$

and if $p : q$ is in its lowest terms,

$$k = p, \quad \nu = p-q, \text{ or } q-p, \text{ since } q > p;$$

$q-p$ is therefore the number of independent vertices arising from these terms.

91. The relation of these different sets of vertices may be otherwise exhibited by putting the expression for the inclination into the form

$$\sin\frac{2\pi x}{\lambda}+\sin\frac{2\pi}{\lambda'}(x-\alpha)$$

$$=2\sin\pi\left\{x\left(\frac{1}{\lambda}+\frac{1}{\lambda'}\right)-\frac{\alpha}{\lambda'}\right\}\cos\pi\left\{x\left(\frac{1}{\lambda}-\frac{1}{\lambda'}\right)+\frac{\alpha}{\lambda'}\right\}=0.$$

The zero values of the sine give the $p+q$ vertices of the first set; and the values which make the cosine vanish give the $q-p$ vertices of the other set.

92. Each of these vertices occupies, as in the former case, its special position in the short cycle $q\lambda'=p\lambda$, and lies always on a straight line $y=$ constant when such an exact relation holds.

93. Also, as before, when the above relation is changed into $q\lambda'=p\lambda+\delta$, it may be shown, by examining the successive arguments of the vertices, that they shift their position in successive short cycles, so that they lie on pendulum-curves of long period; also that the period of these curves is, for the $p+q$ system, $p+q$ times that of the Smith's beat, and for the $p-q$ system, $p-q$ times that of the Smith's beat.

94. The curves of both these systems, with the Smith's beats which form part of them, are readily recognized in all those of the pendulum-curve illustrations which approximately satisfy the condition

$$p\mathrm{E}=q\mathrm{F} \text{ or } \lambda'\mathrm{E}=\lambda\mathrm{F}.$$

In the case of the major third, where there are many vertices in each short cycle, and the figure of the short cycle is itself complicated, these curves are not easily recognized. It is necessary to mark a set of corresponding vertices in order to recognize the curve in this case. By the time we arrive at the fifth the curves are quite plain.

The curves of the $p+q$ system are large and bold, extending completely from top to bottom of the illustrations; each curve comprises the bow of a Smith's beat both above and below. These may be spoken of as the external system.

The curves of the $q-p$ system are smaller, and lie nearer the axial line of the illustrations. These may be spoken of as the internal system. In the particular case where $q-p=1$,

such as $q=2$, $p=1$, the internal system exhibits complete periodic curves having the period of the Smith's beat.

95. Case III., where F is so small that qF is small compared with pE. This would fall under the argument of the first case, with the signification of the letters reversed. But as we made the convention $q>p$, there arise some special points of difference.

96. Where q is much greater than p, as is the case of high harmonics combined with a fundamental, F has to be very small indeed in order that qF may be small compared with pE. In this case, unless F is almost evanescent, it is not generally true that the only vertices are those of E (the fundamental); for in these cases the vertex of the fundamental curve becomes almost a straight line in the short space occupied by a wave of the higher curve; and under these circumstances the vertices of the higher curve continue to be visible wherever they come upon the vertex of the lower, especially where the two vertices are turned opposite ways.

The conditions of case I. not being strictly fulfilled, the consequences there deduced do not strictly follow. The considerations as to the number of different vertices which develop curves are not materially affected. And it remains true that there are always p curves (in case I. q curves) actually developed; but it is not true that there are no traces of any of the other q curves of the entire external set of $p+q$ of case II. On the contrary, it is seen in several of the illustrations, where for the most part $p=1$, that, instead of the outline being one pendulum-curve embracing the outlines of all the Smith's beats, the internal vertices of the long curves present traces of the crossing of two pendulum-curves of longer period—an effect which is seen to survive from the more general cases, on comparing the illustrations to case II. As the amplitude of the higher note diminishes, this curve assumes a trochoidal form, the external vertices being less sharp than the internal, where there is the survival from the crossing. Ultimately, no doubt, the outline would become theoretically a pendulum-curve. But, in the case of indefinite diminution of the coefficient $\frac{q\mathrm{F}}{p\mathrm{E}}$, where $\frac{q}{p}$ is great, $\frac{\mathrm{F}}{\mathrm{E}}$ is of the order of the product of two small quantities; consequently the effects on the displacements, or

the curves we are examining, would themselves tend to become evanescent before their peculiarities; consequently the curve enveloping the Smith's beats would never in this way be reduced to a pendulum-curve having the period of those beats.

In the application of these considerations we have, further, to remember that the resultant tones which present pendulum-curves having the periods of Smith's beats are only heard when both notes are pretty loud; and under these circumstances the indefinite diminution of the ratio above supposed is not admissible. The only case, therefore, in which a locus of vertices is a pendulum-curve of the same complete period as the period of Smith's beat, is that of an internal system under case II., where $q-p=1$. As the existence of this system depends on the accurate adjustment of the coefficients to the law $p\mathrm{E}=q\mathrm{F}$, it cannot be referred to even as an illustration of a phenomenon of general occurrence.

97. We conclude, in conformity with the explanation at the end of the former part, (1) that the forms exhibited by the resultant of two pendulum-curves do not, as a rule, exhibit any appearances corresponding to pendulum-curves having the period of the Smith's beat, except in a very small number of cases, the conditions for which can only be fulfilled by accident; (2) that the increases and diminutions of the maximum displacement which form what we have called the bows of the harmonic curves, correspond in duration with the Smith's beat, but not in the period of the harmonic curves of which they form part.

98. We infer from the previous parts of this paper:—(3) that the variations of maximum displacement which are represented in these figures by the bows of the harmonic curves, give rise by transformation to pendulum-vibrations having the same frequency as those variations—these being the notes which König calls beat-notes, and Helmholtz difference-tones of various orders; and (4) that the actual beats of mistuned consonances of the form $h : 1$, as heard by the ear, are given rise to by the interference of these beat-notes or difference-tones with the lower note of the combination.

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99. The upper numbers prefixed to the Plates of curves are

the ratios of the wave-lengths; the lower ones the ratios of the amplitudes.

Typical curve of case I. . $\frac{27}{80}$
9 : 8

Typical curve of case II. . $\frac{27}{80}$
3 : 1

Typical curve of case III. $\frac{27}{80}$, or rather $\frac{1}{3} \times \frac{80}{79}$
9 : 2 10 : 1

POSTSCRIPT.—The curves shown in the Plates are all illustrations of the subject of this paper, with the exception of three sets; namely, the combinations of vibrations whose wave-lengths are nearly as 4 : 5, as 2 : 3, and as 2 : 5. These have been given for the sake of completeness in the collection of curves, and that readers may have the opportunity of seeing the nature of the difference between such curves as these, which may be said to belong to mistuned consonances of the form $h : k$, and our normal forms which belong to mistuned consonances of the form $h : 1$.

XXV. *On the Transmission of Radiation of Low Refrangibility through Ebonite.* *By* Capt. ABNEY, *R.E., F.R.S., and* Col. FESTING, *R.E.**

WHEN Mr. Graham Bell described his interesting experiments with the photophone, we were much surprised to learn that an effect was produced when sheets of ebonite of small thickness were interposed between the apparatus and the source of radiation; and it became a matter of more than curiosity to us to know what was the cause of the phenomenon, since photographic manufacturers were commencing to use ebonite in the construction of the dark slides for the camera.

We think we can demonstrate, however, that the ordinary explanation of transmission of radiant energy can account for the phenomenon. Dr. Guthrie kindly furnished us with a sheet of ebonite, through which the action of a beam of

* Read April 9, 1881.

radiation on a selenium cell was most marked; and we accordingly first experimented with that. A photographic spectroscopic apparatus was employed, of the form we have already described in other papers; and the compound of silver was used which is sensitive to all parts of the spectrum. At first we employed only one prism, and used the sun as a source of illumination; and here it may be parenthetically remarked that on the evening when we made our first experiments the wind was blowing from the north-east, and there was a clear sky. Half the slit was covered up, a piece of ebonite placed in front of the other half, and a plate exposed to the action of the spectrum of the radiations (if any) coming through this thin layer of apparently opaque matter. An exposure of three minutes was given; the exposed half of the slit was then closed and the other half opened, and a spectrum taken through a solution of bichromate of potash $\frac{1}{10}$ inch thickness. This bichromate was used to prevent the too energetic action of the more refrangible rays, which illuminated the prism and would have caused a veil over the plate. Half a minute's exposure was given. The plate, on development, revealed that rays of very low refrangibility had passed through the ebonite, commencing at W.L. 12,000 and extending as far as W.L. 7500; the point of maximum intensity was situated at about 9000. The photographs were on a small scale, but sufficed to show the absorption of the ebonite. On the next day we had intended to repeat the experiments with two or three prisms; but the wind had shifted, and the solar spectrum was absorbed as far as about 9000, showing the presence of aqueous vapour. It was therefore useless to experiment further with the sun as a source of radiation; so we used the water of the positive pole of an electric light as a source. It will be seen that the spectrum through ebonite extends to about W.L. 15,000, and then terminates.

The next point to determine was as to the quality of the beam coming through the ebonite. This we determined as follows—first by placing a piece of ebonite in contact with the photographic plate and throwing an image of the points on it, and thus getting an impression, and then, by a simple arrangement, removing the ebonite to a distance of 1 foot, and allowing the beam to traverse it, and securing another image on a different plate. The photographs showed that the rays are

very much scattered in their passage through the ebonite, no distinct image being formed in the latter case, though it was sharp and defined in the former. The amount of scattering it seemed desirable to know. For this purpose the collimator of the spectroscope was used and no prism, the image of the slit $\frac{1}{20}$ inch wide was focused on the focusing-screen of a camera, and a piece of ebonite was placed in contact with the plate, and exposure made. This piece was removed and another piece inserted $2\frac{1}{2}$ inches in front of the plate, and another exposure given. The diffusion was most marked: a line $\frac{1}{20}$ inch broad was diffused over a space $\frac{1}{4}$ of an inch, most intense, of course, in the centre. By subsequent experiment it was shown that an exposure of three times the length of that given in the first case was necessary to cause the central portion of the band in the second case to correspond in intensity with that of the image of the slit in the first case. With two pieces of ebonite in contact with the plate six times the exposure was required to give the same intensity as with only one plate of ebonite intervening. Hence we may say that the coefficient of absorption of a plate of ebonite $\frac{1}{64}$ of an inch in thickness $=1{\cdot}8$; and a calculation will show that any rays which can penetrate through $\frac{1}{8}$ of an inch of ebonite will only have an intensity of $\frac{1}{1650000}$ that of the resultant beam, without deducting any thing for the scattering of light. In fact, with the electric light and a wide slit an hour's exposure produced no effect on the photographic plate when ebonite $\frac{1}{8}$ in. in thickness was placed before the slit. It must, however, be remembered that ebonite varies in quality; sometimes the outside alone is black, the inner portions resembling gutta percha in colour. With specimens of this sort a greater thickness could no doubt be traversed than $\frac{1}{8}$ inch. In such a case, however, we doubt if the substance would be true ebonite.

In a communication to 'Nature,' Messrs. Ayrton and Perry show how they determine the refractive index of ebonite by an arrangement with the telephone. They use a prism; and we should judge by the figure they give that the thickness of ebonite traversed must be about $\frac{1}{4}$ of an inch; so that the radiations transmitted must be very small. We may remark that the direction of a beam of light issuing from a prism formed of a turbid medium would not have its maximum in-

tensity in the true direction of refraction ; it would be slightly displaced. Mr. Preece, in a recent communication to the Royal Society, remarked that some ebonite he tried was as transparent as rock-salt; and so it is if a thin-enough layer be taken; and we think that it was the minute layer that was taken that caused this expression to be used. He also stated that another sample equally thin was perfectly opaque to radiation. Through his kindness we were able to experiment with the identical samples to which he refers. The "transparent" specimen behaved as that we have already described; the opaque one showed that the radiations were more scattered in their passage through it. We may state that, by examining the thin ebonite with which we first experimented, we could see a trace of the sun's image through the material, and very faintly through two layers. The radiations of low refrangibility were evidently more copiously passed, since when an image of the sun formed by a lens was caused to fall on a piece of paper and a sheet of thin ebonite interposed, if the eye or hand was placed at the focus considerable warmth was felt.

It became interesting to know whether the ebonite was merely a mechanical mixture of sulphur and india rubber or a chemical combination. Placing a piece of stout india rubber, about the same thickness as the ebonite, before the slit of the spectroscope, and with an exposure of ten minutes, no vestige of an image was found on development of the plate. This was evidently owing to the great scattering of the rays by the substance. The india rubber being laid in contact with the plate, and an exposure made through it, showed that it was transparent to all rays from 10,000 to 5000. The absorption-spectrum therefore differed; and it is evident that in ebonite the india rubber is chemically changed in composition.

The conclusion to be drawn is, that ebonite, when of small thickness, transmits to some extent the rays of low refrangibility.

XXVI. *Note on Stereoscopic Vision.*

By Professor Helmholtz*.

The motives by which we judge the distance of the objects before us with one eye are the following:—

1. The outlines of the more distant objects are covered by those of the nearer, where they meet. It is this circumstance which causes the difficulty we have in recognizing the fact that the image projected by a convex lens or a concave mirror is nearer to the observer than the lens or the mirror.

2. The object which throws a projected shadow upon any surface is situated always before that surface. These first two motives are very rarely overpowered by any other ones —as, for instance, by stereoscopic combination. This is easily demonstrated by Dove's pseudoscope, an instrument containing two rectangular prisms, and showing to each eye a reflected image inverted from right to left. It produces an inverted stereoscopic effect if there are no projected shadows, and no outline covered by the outline of a nearer body.

3. If the head is moved to the right or the left, upwards or downwards, the direction of the eyes remains steady if the object observed is infinitely distant, but is altered the more the nearer the object is. If the head is brought nearer to the object, the convergence of the eyes increases; if it is moved backwards, the convergence diminishes.

We may call the peculiarity of the eye producing these phenomena the *parallax for motion of the head.* At the same time the relative situation of objects of different distance in the field of vision is altered. Distant objects apparently go with the observer, nearer objects in opposite directions. Also this overpowers stereoscopic combination. In Brewster's stereoscope the two images are brought together with a moderate convergence of the eyes, but are nearly in the focus of the lenses, so that these project images at an infinite distance. The instrument is adapted to presbyopic vision. But if it is fastened to a table and the head of the observer is moved, the objects appear to be far more distant than the point of convergence.

I concluded from this and similar observations that the per-

* Read April 9, 1881.

ception of the absolute convergence of our eyes is very indistinct, and that only differences of convergence, related to apparently near or distant objects, produce the stereoscopic effect. But lately I have observed that certain apparent motions of binocular objects may be observed, which prove that the incongruence between the degree of convergence and the parallax of motion is perceived with great accuracy.

The easiest way to see them is the following :—Look to a papered wall, the pattern of which is regularly repeated at distances not much greater than the distance between your eyes (between 60 and 70 millim.). You know that it is possible to make your eyes converge either to a nearer or to a more distant point than the surface of the paper ; so that in your binocular field of vision two images get corresponding position, which do not belong to the same part of the paper, but to two different copies of the pattern. You see, then, a stereoscopic image of the pattern, either more distant and of greater apparent size, if you diverge your eyes, or nearer and smaller, if you converge. But the appreciation of the apparent distance of this pattern is not very precise. If you try to bring a pencil to the apparent place of the nearer pattern, you will find that the point of convergence is far nearer than the apparent place of the pattern.

When you now move your head the pattern moves also. If you have increased the convergence of the eyes, the pattern moves with the eyes, as well to the left and the right as up and down and forwards and backwards. If you diverge, it goes in opposite direction to your head.

XXVII. *Note on Thermal Electrolysis.*

By J. H. Gladstone, *F.R.S.*, *and* Alfred Tribe.

During the course of our experiments on metallic replacements we noticed that some sheet silver, immersed in fused silver chloride, became quickly studded with crystals of metal. A replacement of a metal by itself seemed so anomalous, that our first idea was that the silver employed

* Read April 9, 1881.

contained certain impurities; but we found that the action took place just as well with the purest silver we could obtain, and that it was not restricted to the substances above mentioned. Not only might the iodide of silver be substituted for the chloride with the same result, though not so rapidly effected, but other metals might be employed. Thus, when copper was immersed in fused cuprous chloride, crystals of that metal separated; and similar exchanges took place when zinc was placed in melted zinc chloride, or iron in ferrous chloride in a molten condition.

It was then thought that a different physical condition of the rolled metals might give rise to the action; but this was disproved by the following experiments:—

Some crystals of silver prepared by electrolysis were placed in the open end of a piece of glass tubing slightly constricted, and then immersed in silver chloride heated in a crucible by a Bunsen lamp. In about half an hour the crystals were found to have grown in a net-like mass from their original position to a point about half an inch higher in the tube. This experiment was repeated with crystals of silver which had themselves been deposited from the fused chloride by means of metallic silver. A similar result was obtained.

We were then led to the conclusion that the change depended upon the unequal heating of different parts of the immersed metal, or rather of the salt in which it was immersed. It is evident that upon the contact theory of voltaic action, there will be a difference of potential between the metal and the liquid chloride with which it is in contact; and it is in accordance with analogy to suppose that this difference of potential will vary according to the temperature. Now, under the conditions of the experiment, it cannot be supposed that all parts of the fused chloride in contact with the immersed metal were always equally heated; and we have therefore the possibility of a current being established with the consequent electrolysis of the salt.

In order to test this view, some silver chloride was fused in a hard glass tube and a rod of silver placed in the liquid. On heating the underside of the lower end for 10 minutes, we found a considerable crop of silver crystals in the comparatively cool part of the fluid.

In another experiment some silver chloride was fused in a crucible, and one side of the vessel was more strongly heated than the other. Two long rods of silver were connected with a galvanometer and placed, one in the hotter, the other in the colder part of the chloride. The latter was found studded with crystals at the end of 15 minutes, whilst the former was quite clean. On repeating this experiment, it was always found that the galvanometer gave a larger deflection the greater the difference of temperature between the portions of the fused mass penetrated by the silver wires, and that the current was reversed with a reversal of the rods. Copper wires in cuprous chloride gave similar results.

In an experiment with an electrometer we obtained a clear indication of a difference of potential between silver rods in hotter and colder parts of silver chloride fused in a small crucible, the deflection showing a difference of possibly $\frac{1}{50}$ of a volt. The reversal of the rods again produced a reversal of the deflection.

In corroboration of the theory above stated, it should be borne in mind that the chlorides of silver, copper, zinc, and iron, when fused, are electrolytes. The liquid chloride of tin is not an electrolyte; and it was found that on immersing tin in this liquid no deposition of crystals was observed when it was so arranged that one part of the liquid was kept at the heat of boiling water and another at the ordinary temperature for two days; nor was there the least action on a galvanometer when arrangements were made for testing by that instrument.

These experiments form a good lecture-table illustration of the conversion of heat into electricity and chemical force. They also seem to have a bearing on the theory of voltaic action, since, from the nature of the substances employed, it is difficult to imagine that chemical action in any way initiates the current.

PROCEEDINGS

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[II. *On the Ascent of Hollow Glass Bulbs in Liquids.*

By EDMUND J. MILLS, *D.Sc., F.R.S.**

EN a hollow glass bulb is detained at some depth the surface of a liquid and then released from its ı, it rapidly acquires a sensibly uniform velocity; ı motion continues to be characterized by such velo- ıtil the surface is reached or nearly reached, the r at that time being much accelerated. The bulb next mewhat out of the liquid and then falls; oscillating ntil it finally comes to rest under the usual conditions ating body. In the present paper I propose to give ıunt of an experimental investigation which has refer- the stage of uniform velocity.

he bulbs I have generally employed consist of ass, and have, as will be seen in the accom- g figure, a somewhat pyriform shape; the rminates in a hook, which carries an adjusted eight. A few small projections are sealed on ıody of the bulb in order to prevent too close tal contact with a wetted boundary. In work- h these bulbs, I have always effected the de- ı with a piece of glass tubing, and find that

Fig. 1.



Scale ½.

* Read May 14, 1881.

after some practice, it is seldom an experiment is lost by lateral divagations of the bulb. It is necessary that all the surfaces be clean.

I. *Change of the Diameter of the Reservoir.*

3. A series of glass cylinders having been selected, their mean diameters between two fixed marks 220 centimetres apart were determined. These marks were ruled at places sufficiently distant from the surface and bottom of the liquid to ensure the uniformity of the motion observed between them. The liquids were first heated a little above the temperature desired for the experiments, then poured into the cylinders; and these were immersed in a much larger glass vessel containing water of very nearly the same temperature. The thermometers used could be read directly to tenths, and to hundredths by estimation. The times were taken with a metronome beating thirds of seconds.

4. The following experiments were made at 16° with a mixture of alcohol and water of sp. gr. ·9120 at that temperature; they are compared in the table with numbers calculated from the equation

$$\left.\begin{aligned}(t-\tau)d^2&=c,\\(t-6{\cdot}10)d^2&=23{\cdot}59.\end{aligned}\right\}$$

TABLE I.

d.	t obs.	t calc.
5·66	6·56	6·84
4·76	6·83	7·18
3·37	8·17	8·18
2·79	8·62	9·13
2·20	12·08	10·97

Probable error of a single experiment, 0·44.

The experiments were actually made on a height of 11 centim.; and the values obtained for t were half those given in the table. Each result is a mean of seven determinations.

From the above comparison, it appears that the product of the number of seconds t (less a constant τ) into the square of the diameter d of the cylinder is a constant quantity c. The time of ascent through a cylinder of infinite diameter would have been $\tau = 6{\cdot}10$ seconds. The law, however, shows indications of failure when the diameter is narrowed to 2·2 centim.

5. Table II. contains the results of some experiments with recently-boiled water, at 15°, and another bulb. The time is calculated to seconds. Each result is a mean of these determinations.

TABLE II.

d.	t obs.	t calc.
17·16	26·2	26·17
9·24	26·1	26·71
5·66	26·3	27·97
4·76	27·7	28·80
3·37	29·9	31·63
2·79	37·6	34·24
2·20	41·0	39·20

Equation, $(t-25{\cdot}95)d^2=64{\cdot}56$.

Probable error of a single experiment 1·29.

Sum of the errors (t obs. $-t$ calc.), +0·08.

The last two numbers suggest the same remark as in (4).

6. A sample of hydrocarbon-oil was next tried, a different weight and bulb being used. Each result is a mean of six determinations. The sp. gr. of the oil was ·9120 at 16°, *i. e.* the same as that of the mixture of alcohol and water referred to in (4).

TABLE III.

d.	t obs.	t calc.
5·66	31·5	31·41
4·76	35·3	34·91
3·37	46·0	46·80
2·79	57·4	57·73
[2·20	90·8	78·88]

Equation $(t-22{\cdot}96)d^2=270{\cdot}65$.

Probable error of a single (1–4) experiment, 0·37.

II. *Change of the Unbalanced Pressure.*

7. The unbalanced pressure, to which the ascent of the bulb is due, can be conveniently changed by increasing or diminishing the weight attached to the bulb. If we take a centimetre as the unit of volume, and understand by δ the mean density of (bulb + contents + weight) referred to that of the

liquid as unity, then $(1-\delta)=p$ may be termed the "unbalanced unit pressure."

The following experiments were performed with a bulb of the usual size, recently-boiled water at 11°·5 being the liquid. The diameter of the cylinder was 5·66 centim.; the times are stated in half-seconds; and each result is the mean of seven determinations.

TABLE IV.

t.	p.	tp^2.
20	·01139	·0025946
40	·00810	·0026244
81	·00569	·0026225

Equation, $tp^2=c=$·0026138.

Probable error of c, 0·25 per cent.

8. Another set of experiments was carried out in the same cylinder, under nearly the same conditions, with five variations of weight. Each result is the mean of five observations of ascent through a height of 16·5 centim. The times are stated in thirds of seconds.

TABLE V.

t.	p.	tp^2.
15·5	·00438	·00029735
31·0	·00310	·00029791
60·0	·00223	·00029844
97·0	·00177	·00029705
146·2	·00143	·00029806

Equation, $tp^2=c=$·00029776.

Probable error of $c=$·000000169=0·06 per cent.

The product of the square of the unbalanced unit pressure into the time is therefore a practically constant quantity.

III. *Change of Content.*

9. In all the experiments above recorded the bulb contained air, probably at a pressure slightly below that of the atmosphere. The mean density of (bulb + contents + weight) is of course affected by the contents of the bulb, and then also the rate of ascent.

If we regard as correct the mathematical relation last

arrived at (8), it is easy to deduce from it an equation which involves the specific gravity of the contained gas. Assuming other conditions to remain unchanged, the density of the gas is

$$\gamma = A + B\sqrt{\frac{t-\theta}{t}}.$$

In this expression t is the time of ascent through the constant height for any particular gas, θ the time of ascent corresponding to a gas of density A, and B the density of a gaseous content which just fails to let the bulb sink. It is convenient to put $A=0$, which corresponds to the bulb being vacuous; B and θ are then deduced, as the "constants of the bulb," from two independent determinations.

10. In order to change at pleasure the contents of the bulb its form was slightly altered, as shown in fig. 2, and its volume enlarged. The two stoppers with which it was furnished were coated, on their ground surfaces, with a scarcely perceptible film of grease; the operator's hands were encased in gloves; and every experiment was carried out as speedily as possible. The gases were employed in the dry state, at an average barometric pressure of about 75·7 centim.; in the following table their densities are referred to hydrogen. Each result is a mean of several determinations; and the times are given in thirds of seconds.

Fig. 2.



Scale ½.

TABLE VI.

Gas.	γ found.	γ.	t.
Carbonic dioxide ...	21·81	22·00	72·5
Oxygen	17·17	16·00	38·2
Air	14·13	14·50	30·6
Water-gas	6·44	6·00	23·0

The equation is $\gamma = 26{\cdot}032\sqrt{\frac{t-21{\cdot}589}{t}}$.

Probable error of a single comparison, 0·51.

Great accuracy in work of this kind is, of course, out of the question; but for approximate determinations, when only very small volumes of a gas are available, the method will probably be advantageous.

11. The following set of experiments has reference to a medium consisting of two mixed liquids, the rate of ascent of a bulb in each of which separately is known. One of the liquids was castor-oil, the viscosity of which is very considerable; to 100 parts of this, successive quantities z of linseed-oil were added so as to gradually reduce the viscosity. The uniform temperature was 12°·4. By separate experiments with the oils it was found that, if t were the rate of ascent of the bulb in seconds per centimetre, λ the rate for linseed, α the unbalanced unit pressure in castor, and β the change in that pressure for every unit of linseed added, then

$$\left.\begin{aligned}(t-\lambda)(\alpha+\beta z)^2&=c,\\ (t-\cdot32335)(\cdot09122+\cdot00169z)^2&=\cdot034376,\end{aligned}\right\}$$

are equations which fairly represent the experiments.

TABLE VII.

t.		z taken.	z calc.
4·45454	.....	0·0	0·0
3·10027	.....	11·1	11·9
2·21798	.....	25·0	25·7
1·52758	.....	42·9	46·0
1·22140	.....	66·7	61·8
0·32335	.....	∞	∞

Probable error of a single comparison, 1·7.

Sum of the errors, +0·3.

12. Castor-oil presents the remarkable property of recovering its normal viscosity very slowly after heating. A sample of the oil, through which a bulb rose in a known number of seconds per 22 centim., was heated to a temperature not exceeding 80°, and cooled to its previous condition. The bulb now took ten seconds less for its ascent. After a day's repose it rose again in the oil with its original velocity.

13. The fundamental formulæ given in this paper admit of easy extension to other cases. I have, for example, found in the ascent of a hollow glass bulb a good indication of the maximum density of water, and of the amount of dissolved matter in saline solutions; and it could obviously be applied to determine the specific gravity of solid bodies.

The experiments which I have recorded show clearly that

the rate of ascent of a solid through a liquid depends, not only upon the density of the liquid, but upon some other property —probably the viscosity. When the ascending solid approximates in diameter to the diameter of the reservoir, special retardation occurs, and some new law controls the motion. The commencement of this retardation is earlier with oils than with water, earlier with water than with alcohol and water—earlier, in short, when viscosity is greater. In reservoirs of sufficient diameter, the rate is inversely proportional to the square of the altered condition.

My thanks are due to Messrs. Ellis and Smith for their aid in this investigation.

Glasgow, March 1881.

XXIX. *Change of State: Solid-Liquid.* *By* J. H. Poynting, *Late Fellow of Trinity College, Cambridge, Professor of Physics, Mason College, Birmingham.*

[Plate XIII.]

Two distinct types of change of state from solid to liquid have usually been recognized. The most familiar of these is the ice-water type, in which, as the temperature rises, the solid remains quite solid up to the melting-point; when this is reached it begins to melt *at the surface*, and the temperature remains constant till the whole is liquid, when the temperature again rises. Corresponding to this change of state there is a definite latent heat. In the second class of bodies, of which sealing-wax and phosphorus are examples, there is a gradual softening as the temperature rises; and this softening takes place *throughout the mass*. There is no definite arrest of the rise of temperature, and no definite latent heat.

It has sometimes been supposed that the ice-water type is merely a limiting case of the sealing-wax type, where the softening takes place, but through a very small range of temperature. Prof. Forbes held this view, and by it attempted to explain regelation; but subsequent experiments have not supported the theory, and I believe it is now generally abandoned.

Since, in the ice-water form of change of state, fusion only

takes place at the surface, it seems much more probable that it is an exchange phenomenon analogous to the change which takes place when water is evaporating, according to the kinetic theory. Just as in the case of water-steam, a steady state is reached when the number of molecules escaping from the surface of the water into the gas is equal to the number passing from the gas into the water, so in the case of water-ice a steady state (that is to say, the melting-point of ice) is probably reached when the number of molecules passing from the ice into the water is equal to the number passing from the water to the ice. For the analogue of the sealing-wax type of melting we must probably take the change of state which takes place in a liquid-gas above its critical point, where it changes gradually from a state rather liquid than gaseous to a state certainly gaseous.

In this paper I shall attempt to support this view of solid-liquid change of state. The following is a summary of the argument and the conclusions arrived at.

It is assumed that the maximum vapour-tension of a substance at any temperature is an indication of the number of molecules crossing its surface in a condition to escape. Now Regnault's experiments show that at 0° ice and water have the same vapour-tension; that is, the number of molecules crossing the surface of the ice ready to escape is equal to the number crossing the surface of the water in the same condition. Hence, when the two are in contact at 0°, the interchange of molecules is equal. For temperatures below 0°, Kirchhoff has shown that the vapour-tension of water is greater than that of ice, and above 0° it is less than that of ice—if ice can exist. (Another proof of this theorem is here given.) It is, then, easy to give a general explanation of the phenomena of melting and freezing by supposing that, if the temperature is not at the melting-point, the substance in the state with the greater vapour-tension will lose at the expense of the state with the less vapour-tension.

To explain the alteration of the melting-point by pressure, we must suppose that pressure alters the vapour-tension, and therefore the rate of escape of molecules, and that this alteration is different for the two states. Sir William Thomson has shown that a liquid in a capillary tube is in equilibrium with

its vapour at a greater or less tension than at the plane surface according as the surface is convex or concave, upwards, and has given a formula for the difference. Accompanying this curvature of surface is a difference of pressure in the liquid; and I suppose the variation of vapour-tension to be due to the difference of pressure. A proof is given of Sir W. Thomson's formula, which seems to bring out more clearly the connexion of the phenomenon with the pressure, and which seems to apply to solids as well as liquids. According to this formula, the steady state (the melting-point) may be reached at any temperature if the pressure can be so adjusted that the vapour-tensions in the two states at that temperature and pressure are equal. The resulting lowering of the melting-point by pressure agrees in amount with that given by the well-known formula of Prof. J. Thomson.

It follows from this mode of regarding the subject, that, if in any way the ice can be subjected to pressure while the water in contact with it is not so subjected, then the lowering of the melting-point per atmosphere is about 11½ times as great as when both are compressed. I give the results of some experiments which I have made to test this, and which certainly seem to indicate that the fall of melting-point is much greater than the amount usually supposed if the ice alone be compressed.

The isothermals for ice-water are then discussed. It has been supposed that, if we could employ a sufficiently low temperature and high pressure, then ice would pass continuously into water; that is, the isothermals would have no horizontal part corresponding to a mixture of ice and water, and we should have a critical point. Assuming, however, that a mixture of ice and water completely freed from foreign gases can be subjected to great negative pressure or tension, it seems probable that there is another critical point at a temperature above 0° and at a high negative pressure; that is, the water-ice line is a closed curve. We know that below 0° the water isothermals can be prolonged below the horizontal portion, since water is unfrozen in certain cases,—and that the ice isothermals can be prolonged above the horizontal portion; for ice, at 0° say, can be suddenly compressed without melting in the interior. This suggests that the true form of the isothermals

is a continuous curve, of the nature which Prof. J. Thomson has suggested in the case of liquids and their vapours.

If we suppose that the curves are continuous in the same manner for ice-water above 0°, then Prof. Carnelley's "Hot Ice" would seem to be represented by the prolongations upwards of the ice isothermals beyond the horizontal line to where they meet the line of no pressure. The critical point, which certain assumptions roughly fix at about 14° C., would then be an upper limit, or rather above the limit, to the temperature of hot ice in a vacuum.

In conclusion, it is pointed out that the sealing-wax type of melting is probably similar to the change of ice into water below the lower, or above the upper, critical points, if these exist.

Melting and Freezing of the Ice-water Type at ordinary Temperatures and Pressures.

It seems to have been conclusively proved by experiment that, in bodies of the ice-water type, change of state, either from solid to liquid, or the reverse, takes place only at the surface, or at a surface separating dissimilar portions. This would also seem to follow from the fact that the change of state always requires a certain finite amount of energy to be abstracted from, or supplied to, the mass without alteration of temperature. In the middle of a homogeneous body, where the temperature varies gradually, we must have the energy per unit of volume a continuous quantity as we pass from point to point. Hence, when at any point there is sufficient energy per unit of volume to change the state, either the surrounding temperature must be far above the ordinary temperature for change of state, or the surrounding substance must occupy an intermediate condition between the two states. On the former supposition we should certainly not have the ordinary change of state, though something of the sort may occur in the case of Dr. Carnelley's "hot ice;" and in the latter we should have the sealing-wax type, and no signs of this have been observed.

Since, then, change of state is a surface phenomenon, we are led at once to connect it with the escape of molecules which we know to be always taking place from the surface, as indicated by the definite vapour-tension which the body possesses,

whether solid or liquid. Now Regnault's experiments have shown that at 0° ice and water have the same vapour-tension, and at the same time a mixture of ice and water at that temperature maintains the same proportion between the two constituents as long as no heat is allowed to pass into or out of it; that is, as many molecules escape from the water into the ice as pass in the opposite direction from the ice into the water. We seem, then, to be justified in assuming that *the number of molecules coming up to a given surface with a sufficient velocity to escape is indicated by the maximum vapour-pressure at that temperature.*

Now suppose that we have a mixture of ice and water below 0°. Kirchhoff has shown (Pogg. *Ann.* ciii. p. 206) that below 0° the vapour-tension of water exceeds that of ice by ·044 millim. of mercury per degree; and his reasoning will equally prove that it falls below it by the same amount above 0°, if ice can exist at such a temperature. Prof. J. Thomson has subsequently (Brit. Assoc. Report, 1872, p. 24; Proc. Roy. Soc. 1873; 'Nature,' ix. p. 392) arrived at a similar conclusion independently. A proof differing in arrangement from Kirchhoff's, and following out rather the line indicated by Thomson, will be given below.

In a mixture, then, of ice and water below 0°, since the water has the greater vapour-tension, more molecules will cross the surface from the water to the ice than in the opposite direction. The ice will therefore gain, while the water loses. At the same time the molecules will possess less energy when arranged as ice. Hence the temperature of the whole will rise, and this rise will go on till 0° is reached, when there is once more equilibrium—or till the whole is converted to ice, if that condition be previously reached. This seems sufficiently to explain the action of a small piece of ice dropped into water below 0°; and the fact that the change of state is a surface phenomenon seems to show that the presence of some ice is necessary to commence change of state.

If a mixture of ice and water at 0° be supplied with heat, as soon as the temperature rises ever so little above 0° the equilibrium of exchange is destroyed; for the vapour-tension of ice becomes greater than that of water, and therefore the number of molecules entering the water from the ice is greater

than the number going in the opposite direction. But since the water arrangement requires more energy, heat is absorbed, and the mixture has a tendency to fall back to 0°.

Before going on to discuss the effect of pressure on the melting-point, I give a proof, with a somewhat more general result, of Kirchhoff's formula,

$$\frac{d\varpi'}{dt} - \frac{d\varpi}{dt} = \cdot 044 \text{ millim. of mercury,}$$

where ϖ' is the maximum vapour-tension of ice, and ϖ that of water.

Start with a volume v of water at temperature $-t°$. Let it evaporate, always at the temperature $-t°$, in a cylinder which it does not wet, at its maximum vapour-tension ϖ, which we suppose to be maintained by a piston. Let the ultimate volume of the water-vapour be V. Then the external work done in the expansion is $\varpi(V-v)$.

Now let the vapour further expand, always at the same temperature and in equilibrium with the pressure, till we have reached a volume V′ at the maximum vapour-tension ϖ' of ice. Assuming Boyle's law to hold, the work done in this expansion is $\varpi' V' \log \frac{\varpi}{\varpi'}$; and this would be 0 if $\omega = \omega'$.

Now introduce a particle of ice at $-t°$ into the cylinder, and condensation into ice will go on till all the vapour has disappeared. If the ultimate volume of the ice is v', the work done on the substance is $\varpi'(V'-v')$.

Increase the pressure from ϖ' to $\varpi'+p$ till the melting-point is lowered to $-t°$. If κ' is the coefficient of cubic compressibility of ice, $\frac{p^2}{2}\kappa' v'$ is the work done in the compression. Introducing a drop of water, allow the whole to melt into water under the pressure $\omega'+p$, the work done during the melting being

$$(\omega'+p)\{v'(1-p\kappa')-v(1-p\kappa)\},$$

where κ is the coefficient of cubic compressibility for water.

Now let the water expand to its original volume v by gradually reducing the pressure to ϖ. The external work done is $\frac{p^2}{2}\kappa v$.

We now have the substance in its original state; and the cycle through which it has been taken was reversible at every step; therefore

$$\int \frac{dQ}{T} = 0.$$

But T is constant; therefore

$$\int dQ = 0.$$

Then the total external work is zero, or

$$\varpi(V-v) + \varpi' V' \log \frac{\varpi}{\varpi'} - \varpi'(V'-v') - (\varpi'+p)\left\{ v'\left(1-\frac{p\kappa'}{2}\right) - v\left(1-\frac{p\kappa}{2}\right)\right\} = 0.$$

By means of the equation

$$\varpi V = \varpi' V',$$

and neglecting products of ϖ and κ, this reduces to

$$\varpi V \log \frac{\varpi}{\varpi'} = p\left\{ v'\left(1-\frac{p\kappa'}{2}\right) - v\left(1-\frac{p\kappa}{2}\right)\right\} + (\omega-\omega')v. \quad (1)$$

Neglecting the term $(\omega-\omega')v$, and putting for $\varpi' V$ $\omega_0 V_0 \alpha T$, where $\omega_0 V_0$ are the pressure and volume at 0° C., and T the absolute temperature, we have

$$\frac{\varpi}{\varpi'} = e^{\frac{p\left\{ v'\left(1-\frac{p\kappa'}{2}\right) - v\left(1-\frac{p\kappa}{2}\right)\right\}}{\omega_0 V_0 \alpha T}}. \quad . \quad . \quad . \quad (2)$$

For temperatures near 0° C. we may neglect products of p and κ, and we obtain as an approximation

$$\frac{\omega}{\omega'} = 1 + \frac{p(v'-v)}{\omega' V'},$$

or

$$\omega - \omega' = p\,\frac{v'-v}{V'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

At 0°,

$$v'-v = \cdot 087, \quad V' = 209037,$$

and the pressure required to lower the melting-point $t°$ is $\frac{760\,t}{\cdot 00733}$ millim. by the well-known formula. Substituting in equation (3), we get

$$\omega - \omega' = \cdot 044\,t,$$

or

$$\frac{d\omega'}{dt} - \frac{d\omega}{dt} = \cdot 044 \text{ millim. of mercury}, \quad . \quad . \quad (4)$$

which is Kirchhoff's result.

If the temperature be much below 0° C., we cannot make these approximations without further examination, as the terms containing κ and κ' in (2) may rise into importance.

It may be noticed that (2) could be used as an equation to determine p, the pressure required to produce a fall of the melting-point to T, if there were any accurate experimental method of measuring ϖ and ϖ'.

Effect of Pressure on the Melting-point.

If we are right in regarding the change from the solid to the liquid state as an exchange phenomenon in which the rate of exchange is indicated by the vapour-tension, we ought to be able to show that the pressure which lowers the melting-point to a certain temperature will so alter the rate at which the two states of the substance give off molecules from their surfaces, that at that temperature there will be an equilibrium of exchange. That is, we ought to be able to show that pressure alters the vapour-tensions of the two states, but alters them by different amounts, so that the equality of vapour-tensions now occurs at the new melting-point.

Now in the ordinary case, where the vapour-tension is measured we have the substance only under the pressure of its own vapour; but in the rise or fall of a liquid in a capillary tube we may have a substance in contact with its own vapour when the substance is at a very different pressure from the vapour in contact with it.

Sir William Thomson has shown (Proc. Roy. Soc. Edinb. 1870, vol. vii. p. 63; Maxwell's 'Heat,' 1877, p. 287) that if a liquid rises in a capillary tube so that its surface is concave upwards, and (we may add) the pressure of the liquid is less than at the plane surface, then the equilibrium vapour-tension is less than at the plane surface. If the liquid falls in the tube, so that the surface is convex and the pressure greater than at the plane surface, then the equilibrium vapour-tension is greater. It has been supposed that this difference of vapour-tensions is due to the curvature of the surface; and Fitzgerald has suggested that we may thus perhaps obtain a connexion between "two apparently unrelated quantities," the evaporation and the surface-tension (Phil. Mag. [5] viii. p. 384). But while a very slight impurity in a liquid can greatly alter

the surface-tension, it has not been shown that it alters the evaporation to the same degree. I think that we must look for the explanation elsewhere than in the curvature of the surface; and I shall endeavour to show that we may account for the effect by the difference of pressures of the liquid at the curved and plane surfaces. The curvature of the surface is then, as it were, an accidental accompaniment of the difference of pressure, and not the cause of the variation in the vapour-tension. We might therefore expect to find the variation taking place also at flat surfaces if the pressure be altered, and with solid as well as with liquid bodies. We cannot directly investigate the vapour-tension of flat surfaces under pressure; but I shall assume that we may here take, instead, the rate at which exchange takes place when the solid and liquid are in contact with each other.

Sir W. Thomson's formula is

$$p = \varpi - \frac{2T\sigma}{r(\rho - \sigma)}, \quad \ldots\ldots (5)$$

where

p is the vapour-tension in contact with the concave surface,

ϖ is the vapour-tension in contact with the plane surface,

T is the surface-tension of the liquid,

ρ and σ the densities of the liquid and its vapour respectively,

r the radius of curvature of the curved surface.

If P be the difference between the hydrostatic pressures just beneath the curved surface and just beneath the plane surface, equation (5) may easily be put in the form

$$p = \varpi - P\frac{\sigma}{\rho}, \quad \ldots\ldots\ldots (6)$$

or a pressure P in the liquid increases the vapour-tension by an amount $P\frac{\sigma}{\rho}$.

The following proof of this formula, $p = \varpi - P\frac{\sigma}{\rho}$, is, I believe, applicable to both solids and liquids, and obtains a more general form for the result.

Let a volume v of a body (solid or liquid) be in a perfectly conducting cylinder (fig. 1, Plate XIII.) so arranged that the temperature is always constant. A porous plug, which the substance if liquid does not wet, is in the cylinder; and the holes in the plug are to be so fine that any required pressure can be

applied to the liquid without forcing it beyond the further surface of the plug, the curved surface of the liquid there withstanding the pressure. A piston to which pressure can be applied is in contact with the substance; and beyond the plug is another movable piston to which any pressure can be applied, the arrows in the figure indicating the direction in which the external pressures are applied to the pistons.

Let the volume of the substance in the denser state at the pressure of its normal vapour-tension ϖ for the given temperature be v. Let V be the volume of the whole as vapour at the pressure ϖ. Let the equilibrium vapour-tension when the denser state is subjected to a greater pressure $\varpi + \mathrm{P}$ be p, and let the volume of the whole as vapour at the pressure p be V′. Let the coefficient of cubic compressibility be κ. Now take the body through the following cycle.

Increase the pressure to $\varpi + \mathrm{P}$ on the left-hand piston, and then let the substance evaporate through the plug to the right hand, pushing out the piston there at pressure p till the whole is evaporated to a volume V′. If p be greater than ϖ, let the vapour expand from V′, always in equilibrium with the pressure, finally arriving at a volume V and pressure ϖ. Now cover the porous plug, and, if necessary, commence condensation by introducing a small amount of the substance. Push in the right-hand piston at the pressure ϖ till the whole is condensed to volume v.

We have now conducted the substance through a cycle each step of which is reversible*. Then

$$\int \frac{dQ}{T} = 0.$$

* It seems difficult to imagine a plug which would satisfy the condition of reversibility for the solid under great pressure in contact with its vapour. Perhaps the following would answer the requirements, if an ordinary porous plug is insufficient. Suppose the solid in a finely-divided state, and contained in a liquid which wets it but is of a very slightly greater specific gravity, and whose vapour-tension is negligible. During evaporation turn the cylinder with the vapour-chamber upwards. The particles of solid will rise up through the pores, and a small fraction of their surface will protrude, but they will otherwise be subjected to a pressure $\varpi + p$. For condensation reverse the cylinder. As the solid condenses on the surface it will rise up as fast as it is formed, and so increase the volume of the chamber and force back the piston.

But T is constant; then

$$\int dQ=0,$$

and the external work is, on the whole, zero. This gives us

$$\left(\omega+\frac{P}{2}\right)P\kappa v+(\omega+P)v(1-P\kappa v)-pV'-\varpi V\log\frac{p}{\varpi}+\varpi(V-v)=0. \quad . \quad . \quad (7)$$

But since, at low temperatures such as we are here considering, Boyle's law is almost exact, we have

$$\varpi V=pV'.$$

Then, neglecting terms containing $\varpi\kappa$,

$$\omega V\log\frac{p}{\omega}=Pv\left(1-\frac{P\kappa}{2}\right),$$

or

$$\frac{p}{\omega}=e^{\frac{Pv}{\varpi V}\left(1-\frac{P\kappa}{2}\right)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For ordinary values of P this gives

$$p-\omega=\frac{Pv}{V}=\frac{P\sigma}{\rho}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

which agrees with Sir W. Thomson's result in equation (6).

It may be worth while to point out the following result of the reasoning on which the above proof is based.

In a quantity of liquid at a uniform temperature, the number of molecules interchanged across a surface will increase as we descend, owing to the increase of pressure. If near the surface the number be proportional to the vapour-tension at the surface, then at any depth the number will be proportional to the pressure in an atmosphere of vapour at that level which, at the level of the surface, has the pressure of the vapour in equilibrium; that is, the liquid will behave as a non-vaporizing solid through whose interspaces the vapour can move freely.

Assuming, then, that equation (9) holds both for solids and liquids, let us apply it to the case of ice and water in contact with each other at a temperature $-t^\circ$ and at a pressure P, such that $-t^\circ$ is the melting-point.

Let ϖ be the normal vapour-tension of water at $-t^\circ$,
ϖ' " " " ice at $-t^\circ$,
p be the altered vapour-tension of water,
p' " " " ice,
ρ the density of water, v its specific volume,
ρ' " " ice, v' " "
σ " " their vapour, V its specific volume.

Taking σ and V as the same for ice and water as an approximation, then equation (9) gives us

$$\left.\begin{aligned} p &= \varpi + \mathrm{P}\frac{\sigma}{\rho} = \varpi + \frac{\mathrm{P}v}{\mathrm{V}}, \\ p' &= \varpi' + \mathrm{P}\frac{\sigma}{\rho'} = \varpi' + \frac{\mathrm{P}v'}{\mathrm{V}}. \end{aligned}\right\} \quad . \quad . \quad . \quad (10)$$

Subtracting, we have

$$p - p' = \varpi - \varpi' - \mathrm{P}\frac{v - v'}{\mathrm{V}}. \quad . \quad . \quad . \quad (11)$$

But by equation (3) we have

$$\omega - \omega' = \mathrm{P}\frac{v' - v}{\mathrm{V}};$$

then

$$p - p' = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Or, under the pressure P at the melting-point, the vapour-tension of ice equals that of water, and there is an equal interchange of molecules taking place. According to this, then, we may thus regard the alteration of melting-point by pressure. The pressure increases the number of molecules given off from the surfaces in contact with each other in both states; but the increase is greater in the case of the less dense state. Now, in the case of ice-water, ice is the less dense state, and below 0° it has the less vapour-tension. Hence a sufficiently great increase of pressure, while increasing both vapour-tensions, can make that of ice overtake that of water, or can lower the melting-point. For paraffin, the liquid is the less dense state. Then, increase of pressure can only render the two vapour-tensions equal above the normal melting-point when the liquid vapour-tension is less than that of the solid.

Suppose now only one of the two states (the ice) to be subjected to increase of pressure. For instance, let the ice be compressed on a porous plate through which the water can circulate freely. Then the pressure increases the rate at which

molecules escape from the ice into the water, but does not affect the rate of escape of the water-molecules into the ice, and a much less pressure will suffice to produce equilibrium of exchange for a given temperature below 0° than when both ice and water are subjected to the pressure.

To calculate the fall in melting-point produced by a pressure P′ on the ice alone, we have, instead of (10),

$$\left.\begin{aligned} p &= \varpi, \\ p' &= \varpi' + \frac{P'v'}{V}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If we have $p=p'$, we have the melting-point; and in this case, by subtracting, we obtain

$$\varpi - \varpi' = \frac{P'v'}{V}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Now the pressure required to lower the melting-point to the same degree when both ice and water are compressed is given by

$$\varpi - \varpi' = \frac{P \,.\, v' - v}{V}; \quad . \quad . \quad . \quad . \quad . \quad (15)$$

or

$$\frac{P'}{P} = \frac{v' - v}{v}$$

$$= \cdot 087. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Or the fall in melting-point caused by a given pressure on the ice alone is about 11½ times as great as when both ice and water are compressed. That is, 1 atmosphere lowers the melting-point about ·0843° C., and 11·7 atmospheres lower it 1° C. This result may be obtained in the same way as Prof. J. Thomson's formula, on the supposition that the process is reversible; but as I was led to the result by the above considerations, I have given only this proof.

This seems to have an important bearing on ordinary cases of regelation, when two pieces of ice are brought into contact at one or two points. About that point the ice will be subjected to great pressure; but the melted water is not necessarily subject to the pressure, and accordingly the melting-point may be lowered by 11½ times as much as has been formerly supposed.

Perhaps the following imaginary experiment may serve as a simple illustration of the last two sections. Suppose two

cylinders, one containing ice, the other water at the same temperature, to be connected above by a tube through which the vapour can pass, and let them only be in contact with their own vapour.

At 0°, or rather at +·0073, their vapour-tensions being equal, as soon as the pressure reaches 4·6 millim. then the ice and water will remain unaltered in amount as long as no heat is allowed to pass into or out of the cylinders. If the temperature be kept slightly below 0°, then, since the vapour-tension of water is now greater than that of ice, the water will gradually distil over into the ice-vessel and there condense as ice, the average temperature rising. If the temperature be kept constant, however, the whole of the water will in time go over into the ice-vessel. If the temperature be slightly above 0° (supposing it possible still to keep the ice solid), then the ice has the greater vapour-tension and will gradually distil over into the water-vessel, and the average temperature will fall. In time, if the temperature be kept above 0°, the whole of the ice will go over into the water-vessel.

If, now, the ice and water be subjected to pressure by porous pistons which the water does not wet (the pressure in each cylinder being the same), then, if the temperature be 0°, an increase of pressure will cause more evaporation from the ice than from the water; that is, the ice will distil over into the water-cylinder and form water there. To obtain equilibrium again, the temperature must be lowered to such a point that the pressure makes the two vapour-tensions once more equal, when the ice and water will remain unaltered in amount—that is, the melting-point will be reached. If now the ice alone be subjected to pressure, its vapour-tension will be increased while that of the water remains the same. And now the pressure required to produce equilibrium of vapour-tensions at a given temperature below 0° will only be about 2-23rds of that required when both are subjected to the same pressure.

The suppositions which I have made amount to this—that if the space filled with vapour be abolished and the ice and water be brought directly into contact with each other, then the rate of escape of molecules will be the same as before in each case, or bear the same proportion to it.

Isothermals of Ice-water: Critical Points.

If we draw the isothermals for ice and water on a pressure-olume diagram, they are of the general form shown in fig. 2, ough the figure is entirely out of proportion.

If we may assume that the compressibility of water is conderably greater than that of ice, the horizontal part of the othermals representing a mixture of ice and water will in-ease as the temperature falls below 0°, at least just at first. hen, if we call the line passing through the points where the othermals turn to or from the horizontal part the ice-water ne, this line will at first diverge as the temperature falls. low, while ice contracts on cooling, its coefficient of expan-on between −19° and 0° being given as ·000122 by Brunner, lespretz has shown that water expands on cooling below 0° ven more than it expands for an equal rise above 8°. Hence ie isothermals for ice and water approach each other at ordi-ary pressures as the temperature falls.

Using Brunner's coefficient for ice, and for water Hälls-öm's formula (Jamin, *Cours de Physique*, vol. ii.),

$$\frac{v_0}{v_t} = 1 + \cdot 000052939\,t - \cdot 0000065322\,t^2 + \cdot 00000001445\,t^3,$$

nd supposing that water could be cooled without freezing, it ill be found that between −120° and −130° ice and water ould have the same specific volume. This might lead us to spect that the divergence of the two branches of the water-e line would not continue if we could examine the isother-nals at very low temperatures and high pressures, and that, s the temperature fell, the two states would at some point egin to approach (that is, the horizontal part of the isother-nals would decrease), and that ultimately ice would pass gra-ually into water without any abrupt change of volume (that , there would be a critical point). Below this critical point e and water would probably be identical.

A similar conclusion is arrived at from the latent-heat equa-ion. On the supposition that at the critical point the latent eat vanishes, the temperature given by that equation is −122°·5, with a pressure of over 16,000 atmospheres (Baynes, Thermodynamics,' p. 169).

It is usually assumed that we must stop the isothermal at the base-line of no pressure. But we know that water can be subjected to a negative pressure; as, for instance, when it rises in a capillary tube in a vacuum, or when it adheres to a barometer-tube at a height greater than that of the barometric column. It seems probable that, if perfectly freed from foreign gases, it might even be subjected to a very high negative pressure without the particles being torn asunder. So, too, a mixture of ice and water might probably be subjected to tension. It seems at least worth while to draw the isothermals for ice and water on such a supposition.

Prof. J. Thomson's result for the alteration of the melting-point by pressure would hold for at least a short distance above 0° when we replace pressure by tension. Assuming it to hold for 4°, we should have to put on a tension of $4 \div \cdot 00733$ atmosphere = 545 atmospheres. But if the expansion of water under a tension equals its compression under an equal pressure, the expansion is about $\frac{1}{21000}$ per atmosphere*; so that the volume of the water at 4°, under a tension of 545 atmospheres, will be 1·026. The ice, whose volume at 4° under no pressure would be 1·088, probably will not expand nearly so much under tension. The change of volume on melting will therefore probably be not very far from

$$1 \cdot 088 - 1 \cdot 026 = \cdot 062,$$

against a change at 0° of ·087. Then the two branches of the ice-line will converge very considerably for temperatures above 0° and with negative pressures. At this rate of convergence the meeting-point is at about 14° C. At higher temperature the ice would pass gradually into water—that is, we should here have another critical point,—the two critical points being at opposite ends of the closed curve which represents the water-ice line.

On considering the isothermals below 0°, it will be noticed that the water-isothermals, at least as far as that for −20°, can be prolonged downwards past the horizontal line to meet the line of no pressure; for Despretz succeeded in cooling water to −20° in thermometer-tubes without freezing. These pro-

* Might not the truth of this supposition be tested by the propagation of sound through the water above a barometric column at a negative pressure?

longations are represented by $a\,a'$, $b\,b'$, $c\,c'$ (fig. 2). Similarly the ice-isothermals can be at least slightly prolonged upwards past the horizontal line. For, suppose we take a block of ice at 0° and suddenly subject it to great pressure. Since it expands on heating, then sudden compression produces, if any thing, a slight rise in the temperature. At the same time the melting-point is lowered, and the ice begins to melt at the surface, and in time the whole will be lowered to the new melting-point. But just at first, and until it falls to that temperature, we have the ice on the prolongation of the isothermals upwards as at A A′ or B B′ in fig. 2. In a certain sense, then, we have "hot ice."

Since, then, the water-isothermals may be prolonged downwards and the ice-isothermals upwards, we may probably here adopt Prof. J. Thomson's suggestion as to the true shape of the isothermals in the case of liquid-and-gas mixtures (Brit. Assoc. Report, 1871, p. 30; Maxwell's 'Heat,' p. 125). This is indicated by the dotted line for −2° in the figure. If the isothermals also have this shape above 0° (as indicated by the dotted line for the 4° isothermal), then at first the ice-isothermals will be prolonged upwards to meet the line of no pressure, as, for instance, that of 4° at H. This seems to be the place where we must put Dr. Carnelley's "hot ice," on the diagram, if its temperature be really proved to be above 0°.

But if the critical point for the higher temperature exist, it is evident that, before this temperature is reached, the prolongations of the ice-isothermals will cease to reach up to the line of no pressure, and the limit to the temperature of hot ice in a vacuum is that of the last isothermal which touches the line of no pressure. To obtain ice at still higher temperatures, it would apparently have to be subjected to great tension. If the above calculation for the critical point is at all near the truth, then the highest temperature possible for ice in a vacuum is something below 14° C.

The view here advocated as to the nature of the melting of ice, would show that its fixity is as much a "constant accident" as the fixed boiling-point of water. If we have a piece of ice at any temperature and allow no water to form on its surface, then I see no reason why it should melt if heat be supplied to it by conduction from bodies which, when melted,

it does not wet. I think, then, we ought to expect its temperature to rise, as Dr. Carnelley has apparently found to be the case.

Dr. Lodge has pointed out ('Nature,' Jan. 20, 1881) that, as far as we know, "there is no definite subliming-point for a solid, any more than there is a definite evaporating-point for a liquid." Hence, with such a mode of supplying the heat as above described, the temperature might perhaps be expected to rise to that of the last isothermal which reaches the line of no pressure. When it has reached this point the whole will be in an unstable state, and we might expect a further supply of heat to cause a sudden change into water. If, however, at any point in this process of raising the temperature the vapour-tension is allowed to rise nearly to its maximum, it will exceed that of water, which has a lower maximum; then a layer of water will be formed on the ice, and we shall have melting with a tendency of the temperature towards 0°.

The Sealing-wax Type of Melting.

We have seen that there is some reason to suppose that ice would pass gradually into water at a sufficiently low temperature and with sufficiently high pressure; that is, there would be no abrupt change of volume at a constant temperature, and no definite latent heat. But these are just the characteristics of the melting of substances of the sealing-wax type; and I think it exceedingly probable that we have such substances at temperatures below their critical points, or at least that they are analogous to water-ice below its critical point. If sealing-wax have a critical point, then if we start with some in the solid state at ordinary temperature, and while raising the temperature we increase the pressure so as always to keep it solid till above the critical point, if we reduce the pressure again to a certain point and at the same time a small amount of liquid sealing-wax be introduced, we ought to have a liquefaction of the whole with a finite expansion of volume; that is to say, we should have changed the ordinary sealing-wax type of melting into the ice-water type. It might, perhaps, be possible to test the truth of this supposition experimentally.

XXX. *On the Opacity of Tourmaline Crystals.*

By Professor SILVANUS P. THOMPSON, *B.A.*, *D.Sc.**

Introduction.

1. TOURMALINE is distinguished amongst crystals for its remarkable optical properties, particularly its power of polarizing light. It is distinguished moreover by possessing characteristic electric properties. It possesses also a crystallographic interest as furnishing an eminent example of non-superposable hemihedry. There can be little doubt that these remarkable and characteristic qualities are closely related to one another, though as yet very little is known of the nature of this probable connexion. In the present paper an attempt is made to connect the optical and electrical properties of the crystal, by showing that the opacity of the crystal to light polarized in a principal plane of section can be deduced from its electric conductivity.

2. In a paper read before Section A of the British Association at Dublin in 1878, by Dr. O. J. Lodge and myself†, we suggested, as a possible explanation of the phenomena of pyroelectricity in tourmaline, that it might be found to possess unilateral conductivity for electricity—and if for electricity, for heat also. Our experiments on the electric conductivity, however, led to negative results; and in the case of heat-conductivity, the only differences observed of a unilateral kind were such as occurred while the temperature was either rising or falling—not whilst it was constant. Our original suggestion, therefore, was not confirmed, though I obtained instead a result which amounted to the discovery of a new phenomenon, "*the Convection of Heat by Electricity*"—namely, that in a pyroelectric crystal whose temperature is rising, heat flows more easily *with* the electricity than it does *against* the electricity. We were later indebted to Mr. G. F. Fitzgerald, of Trinity College, Dublin, for the suggestion that an analogous phenomenon might occur, namely that there might be a

* Read June 11, 1881.

† Report Brit. Assoc. (Dublin) 1878, p. 495; and Phil. Mag. July 1879.

unilateral electric convection whilst the electromotive force producing the flow was rising or falling*.

3. Whilst we were pursuing these investigations, and before we abandoned our original hypothesis, the suggestion was made to me by Dr. Lodge that if tourmaline possessed unilateral conductivity *along* the axis, this might afford a possible explanation of the greater opacity observed in coloured tourmalines for one set of rays. For if, as on our original hypothesis, the elasticity in one sense along the axis were different from the elasticity in the opposite sense along the axis, vibrations taking place along the axis would be stopped, and the only rays *transmitted* would be those vibrating at right angles to the axis. Unfortunately for this suggestion, the ray whose vibrations are executed in a plane at right angles to the axis is the ordinary ray, which is the one to which the tourmaline is opaque; whilst the ray which it transmits is the extraordinary ray, which, being polarized in a plane at right angles to the axis, is propagated by vibrations (according to Fresnel and Stokes) executed in a principal plane of section. I could not, therefore, agree with this suggestion as to the cause of opacity in tourmaline crystals, though the suggestion that the opacity was involved in the electrical properties of the crystal appeared an extremely likely one.

4. A theory of the opacity of tourmaline crystals, however, has recently occurred to me whilst considering the general relations of electricity and light; and I now beg to offer the following explanation, based upon Clerk Maxwell's electromagnetic theory of light.

According to Maxwell's theory, light is an electromagnetic disturbance propagated in the same medium which transmits other electromagnetic actions, the periodic vibrations being propagated in a wave through media possessing "electric elasticity" (*i. e.* dielectric properties), but being frittered down

* We have not yet put this suggestion to experimental proof. In any case the experiment would be difficult, for the reasons alleged in our paper of 1878. Moreover the question would still be complicated by phenomena of heating; for, as we pointed out in 1878, the phenomena of pyroelectricity must be reversible, and the application of an external electromotive force to a crystal must produce in it a thermal change just the reverse of that which would itself give rise to the electromotive force in question.

into electric currents (and ultimately into heat) when these vibrations pass into conducting media. Good insulators should therefore be transparent, and good conductors opaque, to light. *If it can be shown that tourmaline crystals are better conductors of electricity in one direction than another, it can be deduced as a consequence of Maxwell's theory that they will be better transmitters of light in one direction than in another, and that they will absorb more of those rays of light whose vibrations, consisting of electric displacements, lie in the direction of best electric conductivity.*

The present paper consists of three parts:—

I. A *résumé* of the Optical, Electrical, and Magnetic properties of Tourmaline Crystals.

II. A Mathematical Theory of the Opacity of Crystals which are electrically or magnetically æolotropic.

III. A discussion of the Electric Conductivity of Tourmaline Crystals, and of the Experimental methods of observing it.

I. *Physical Properties of Tourmaline Crystals.*

5. *Optical Properties.*—Tourmaline belongs to the rhombohedral system of crystals, and is therefore optically a uniaxal crystal. Its refractive indices are (approximately)

Ordinary ray 1·6406,
Extraordinary ray 1·6212;

and it is therefore a negative crystal. Tourmalines are of various colours, occasionally colourless, still more rarely pink (rubellite), but frequently bluish-green, green, olive, or brown. The commonest of all kinds is of a brownish tint when cut into very thin slices, but appears exteriorly jet-black. Those of bluish-green or green hue are, according to M. Mascart, the most strongly pyroelectric; and of these the most transparent are more highly pyroelectric than the opaque varieties. *In ordinary light a coloured tourmaline is always found to be much more opaque to rays traversing it in a direction parallel to its axis than to rays traversing it at right angles to its axis, equal thicknesses being considered.* Tourmaline possesses the property of polarizing partially or wholly the light which it transmits. Its action on light is usually explained by saying that a ray of ordinary light incident upon the crystal is divided into two portions, the ordinary and the extraordinary ray,

which in passing through the crystal are unequally absorbed. If a slice of the crystal be taken whose parallel faces are principal planes of section, and which is of a suitable thickness, the ordinary ray will be virtually suppressed, whilst the extraordinary ray is transmitted, though with some loss by absorption. The transmitted ray is polarized in a plane at right angles to the axis of the crystal; and its vibrations are therefore executed (if we assume with Fresnel and Stokes that the vibrations are at right angles to the plane of polarization) in a direction parallel with that of the axis of the crystal.

We may remark parenthetically, that the almost complete opacity of coloured tourmalines to rays travelling along the axis affords a strong confirmation of the views of Fresnel and Stokes. For let this axis be the x-axis of a system of rectangular coordinates, the transverse vibrations to a ray travelling along x must be in planes parallel to the plane (yz); and they are suppressed by absorption whether parallel to y or z. Now for a ray travelling along y the vibrations are in planes parallel to the plane (xz), and the z-component is suppressed by absorption, the x-component only being transmitted; while for a ray travelling along the axis of z the vibrations are in planes parallel to (yx), and, the y-component being suppressed by absorption, the x-component is alone transmitted.

6. *Electrical Properties.*—With the characteristic pyroelectric properties of tourmaline we have not much concern here; for the tourmalines which are most highly pyroelectric appear to be least opaque.

The electric conductivity of tourmaline is in general very small. The resistance of a centimetre cube of the crystal at ordinary temperatures is certainly many thousand ohms. Gaugain states that the resistance decreases rapidly if the temperature is raised to 400° or 500°, and he has observed* some crystals, on being cooled from this temperature, to retain a high surface-conductivity, which he attributed to their *having become* hygroscopic—an explanation which seems somewhat doubtful, since he states that washing them in ordinary water rendered them non-conducting as before. Becquerel sought to explain the disappearance of pyroelectric phenomena at

* *Annales de Chimie et de Physique*, 3e série, t. vii. p. 8.

temperatures above 150° C. by supposing an increase of conductivity to be assumed at that temperature. In the researches of Dr. Lodge and myself in 1878–9 we found no such great decrease in resistance, which at 300° C. was still enormous. We were not able to compare the conductivity in a direction at right angles to the axis with that along the axis.

The only experiment directed toward the comparison of the electric conductivities in different directions with respect to the axis of the crystal, are those of de Senarmont* and of G. Wiedemann†, both of whom examined the conducting-power of the surfaces of crystals. Their methods and results are examined in detail in the concluding part of this paper. They each found the conductivity of tourmaline to be greater along the axis than across the axis: I shall have occasion for showing that this conclusion is fallacious.

7. *Magnetic Properties.*—Plücker examined the magnetic deportment of tourmaline. The following account of what was observed is given by Tyndall‡:—"A plate of the crystal which had been prepared for the purposes of polarization, 12 millimetres long, 9 wide, and 3 thick, was suspended by a silk fibre between the poles of an electromagnet. On sending a current round the latter, the plate, which was magnetic, set itself as an ordinary magnetic substance would do, with its longest dimension from pole to pole. The optic axis of the crystal, thus suspended, was vertical. . . . . On hanging the crystal, however, with its optic axis horizontal, when the magnet was excited, the plate stood no longer as a magnetic substance, but as a diamagnetic; its longest dimension being at right angles to the line joining the poles. The optic axis of the crystal was found to coincide with its length; and the peculiar deportment was considered as a proof that the optic axis was repelled." From all which the logical inference is, that the coefficient of magnetic induction is less along the axis than in a direction at right angles to it. It is curious that Professor Tyndall states§ just the opposite to this—that the maximum magnetic induction is, in coloured crystals at all events, in a direction parallel to the axis.

* *Ann. de Chim. et de Phys.* t. xxviii. (1850), p. 257.

† Ibid. t. xxix. (1850), p. 229; and Pogg. *Ann.* lxxvi. p. 404 and lxxvii. p. 534.

‡ 'Diamagnetism,' p. 2. § *Op. cit.* p. 71.

8. *Thermal Conductivity.*—De Senarmont examined the thermal conductivity of tourmaline by his well-known method. The conductivity is greater across the axis than along it, the ratio between the major and minor axes of the isothermal curves being (according to my own observations) about 3 : 2 and these being proportional to the square roots of the conductivities, we have

$$3 : 2 = \sqrt{k_2} : \sqrt{k_1},$$

or

conductivity along axis : *conductivity across axis* = 4 : 9.

The unilateral conductivity observed in my experiments during rise or fall of temperature need not be further noticed here.

9. *Radiating-power.*—Kirchhoff* and Stewart† have shown that the law of equality of power to absorb and emit radiations extends to the case of the light absorbed by the tourmaline, which, when heated to redness, emits rays partially polarized in a principal plane of section—that is to say, emits those rays most freely which it most freely absorbs.

II. *Mathematical Theory.*

10. Let K, μ, and C stand respectively for the dielectric inductive capacity, the magnetic inductive capacity, and the conductivity per unit of volume of a medium. In crystalline media these quantities will, in general, have different values in three principal rectangular directions, being no longer mere scalar quantities, but linear (and vector) operators upon their several functions. If these values be specified for any crystal, then the optical properties of that crystal may be deduced from the general equations of electromagnetic disturbances. These equations are found in Maxwell's 'Electricity and Magnetism,' art. 783 (7), as follows:—

$$\left.\begin{aligned} \mu\left(4\pi C + K\frac{d}{dt}\right)\left(\frac{dF}{dt} + \frac{d\psi}{dx}\right) + \nabla^2 F + \frac{dJ}{dx} = 0, \\ \mu\left(4\pi C + K\frac{d}{dt}\right)\left(\frac{dG}{dt} + \frac{d\psi}{dy}\right) + \nabla^2 G + \frac{dJ}{dy} = 0, \\ \mu\left(4\pi C + K\frac{d}{dt}\right)\left(\frac{dH}{dt} + \frac{d\psi}{dz}\right) + \nabla^2 H + \frac{dJ}{dz} = 0, \end{aligned}\right\} \quad . . (1)$$

* Pogg. *Ann.* cix. 1860, p. 275. † Proc. Roy. Soc. x. p. 503.

$$J = \frac{dF}{dx} + \frac{dG}{dy} + \frac{dH}{dz},$$

F, G, H are the components of vector-potential at x, y, z) in three rectangular directions parallel to the axes respectively, and where ψ represents the elec-) potential of the possible free electricity. These uations apply to the case of a medium in which both placements and true conduction currents are simul-produced under the action of an impressed electro-ce. They cease to apply in strictness to the case medium possesses movements of its own, which we re considering. If the medium be homogeneous, olotropic or isotropic, and if its conductivity under-scontinuity in its values at any point (that is to say, me continuous values in the same direction), there reason to expect the phenomenon of electric absorp-ur, or free electrification to appear at any internal ie medium. Hence, in considering steady periodic es such as light-waves, we may neglect terms involf-functions of the free electricity, or its volume-den-as $\nabla^2\psi$, since these will be independent of t.

order further to simplify the equations, we will nar-the case to that of a plane wave of unpolarized light l along the axis of z, and therefore lying in planes the plane (xy), in which planes also the electric and isturbances are executed. We will further suppose the der consideration to be, as tourmaline is, a uniaxal d to have its optic axis coincident with the axis of x, e x and y components of the disturbances will be y parallel and at right angles to the optic axis. also make the *assumption* that in tourmaline the r linear vector operators, which should stand for C, may be represented with sufficient accuracy by to these quantities the values

$$K_1, \quad K_2, \quad K_3,$$
$$\mu_1, \quad \mu_2, \quad \mu_3,$$
$$C_1, \quad C_2, \quad C_3,$$

for their respective values as measured in the directions of x, y, and z.

We may then write, neglecting functions of J, which in the case of periodic disturbances can at most be a linear function of the time,

$$\left.\begin{aligned} 4\pi\mu_1 C_1 \frac{dF}{dt} + \mu_1 K_1 \frac{d^2F}{dt^2} + \nabla^2 F = 0, \\ 4\pi\mu_2 C_2 \frac{dG}{dt} + \mu_2 K_2 \frac{d^2G}{dt^2} + \nabla^2 G = 0, \\ 4\pi\mu_3 C_3 \frac{dH}{dt} + \mu_3 K_3 \frac{d^2H}{dt^2} + \nabla^2 H = 0. \end{aligned}\right\} \quad . \quad . \quad (2)$$

Since, however, we are going to deal only with disturbances in the plane (xy) propagated along the axis of z, we may simplify the above to the following form:—

$$\left.\begin{aligned} 4\pi\mu_1 C_1 \frac{dF}{dt} + \mu_1 K_1 \frac{d^2F}{dt^2} - \frac{d^2F}{dz^2} = 0, \\ 4\pi\mu_2 C_2 \frac{dG}{dt} + \mu_2 K_2 \frac{d^2G}{dt^2} - \frac{d^2G}{dz^2} = 0, \\ 4\pi\mu_3 C_3 \frac{dH}{dt} + \mu_3 K_3 \frac{d^2H}{dt^2} = 0. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (3)$$

Or, in words, the rate of change in the transverse components of electromotive force as the wave advances along the axis of z is expressed as the sum of two time-functions of the corresponding components of vector-potential—one of these functions varying with the electric conductivity of the medium, the other with its dielectric capacity, and both being proportional also to the magnetic inductive capacity.

12. We have now four possible cases to consider:—

(i) where K is very great and C relatively negligible, as in non-conducting media;

(ii) where C is great and K relatively small, as in true conductors of electricity;

(iii) where C and K are magnitudes of comparable order, but having different values in different directions.

(iv) where μ has values differing appreciably in different directions.

Although from Plücker's experiments (see § 7 *antè*) it ap-

pears that μ_1 and μ_2 cannot be regarded as equal, yet their values are both approximately so nearly equal to unity that we are not in a position to discuss case (iv).

13. Case i. (*Non-conducting Substance*), C=0.

Equations (2) become

$$\left.\begin{aligned} \mu_1 K_1 \frac{d^2F}{dt^2} - \frac{d^2F}{dz^2} &= 0, \\ \mu_2 K_2 \frac{d^2G}{dt^2} - \frac{d^2G}{dz^2} &= 0, \\ \mu_3 K_3 \frac{d^2H}{dt^2} &= 0; \end{aligned}\right\} \quad \ldots\ldots \quad (4)$$

whence

$$\left.\begin{aligned} \frac{1}{\mu_1 K_1} \cdot \frac{d^2F}{dz^2} &= \frac{d^2F}{dt^2}, \\ \frac{1}{\mu_2 K_2} \cdot \frac{d^2G}{dz^2} &= \frac{d^2G}{dt^2}; \end{aligned}\right\} \quad \ldots\ldots \quad (5)$$

whence it follows that a plane wave in the plane (xy), whose electric displacements are parallel to x, is propagated with velocity V_1; whilst displacements parallel to y are propagated in a wave whose velocity is V_2 with the following values:—

$$\left.\begin{aligned} V_1 &= \frac{1}{\sqrt{\mu_1 K_1}}, \\ V_2 &= \frac{1}{\sqrt{\mu_2 K_2}}. \end{aligned}\right\} \quad \ldots\ldots \quad (6)$$

This agrees with the known fact that a wave of light is split on passing through the crystal into two portions whose vibrations are respectively at right angles to one another, and which move with different velocities.

Now assuming, as above, $\mu_1=\mu_2=1$, we have

$$\frac{V_1}{V_2} = \frac{\sqrt{K_2}}{\sqrt{K_1}} = \frac{\rho_2}{\rho_1}; \quad \ldots\ldots \quad (7)$$

where ρ_2, ρ_1 are respectively the indices of refraction for ordinary and extraordinary rays.

Billet gives (*Optique Physique*, p. 619) the following values for the refractive indices of different specimens of tourmaline:—

Colour of ray.	Ray used.	Ordinary index (ρ_2).	Extraordinary index (ρ_1).	$\frac{\rho_2}{\rho_1}$
Colourless ...	Ray D	1·6366	1·6193	1·0107
Green.....	Ray D	1·6408	1·6203	1·01265
Green-blue...	Red ray	1·6415	1·623	1·01311
Blue	Red ray	1·6435	1·6222	1·01313
Mean		1·6406	1·6212	1·0120

14. From these we deduce for the two velocities of light in tourmaline:—

Ordinary Ray.

$$V_2=\frac{3\times10^{10}\text{ cm. per sec.}}{1\cdot6406}=1\cdot8286\times10^{10}\text{ cm. per sec.;}$$

and

Extraordinary Ray.

$$V_1=\frac{3\times10^{10}\text{ cm. per sec.}}{1\cdot6212}=1\cdot8504\times10^{10}\text{ cm. per sec.}$$

15. The two corresponding dielectric capacities should therefore be

$K_1=\rho_1^2=2\cdot6283$ in direction parallel to crystallographic axis,

$K_2=\rho_2^2=2\cdot6792$ in direction perpendicular to crystallographic axis.

I am not aware of any experimental determination of these quantities having been made.

16. Case ii. (*Conducting Medium*).

Here $\psi=0$, and we may neglect the terms containing K; for, though $K>1$, C is by hypothesis much greater, and the terms containing C are therefore those by which the mode of propagation of electric displacements in the medium are represented. So the equations (3) become

$$\left.\begin{aligned} 4\pi\mu_1 C_1\frac{dF}{dt}-\frac{d^2F}{dz^2}&=0,\\ 4\pi\mu_2 C_2\frac{dG}{dt}-\frac{d^2G}{dz^2}&=0,\\ 4\pi\mu_2 C_3\frac{dH}{dt}&=0,\end{aligned}\right\}\quad\ldots\ldots\quad(8)$$

which are not the equations of any kind of wave-propagation, but represent as going on in the plane (xy) the diffusion of electricity by conduction through the medium at logarithmic rates whose values along the x and y axes are proportional to $-\mu_1 C_1$ and $-\mu_2 C_2$ respectively; that is to say, the disturbances will be propagated just in the same fashion as heat would be in a medium whose thermal conductivities and specific heats had different values in different directions. The spread of electricity in this case resembles therefore that of the spread of heat in a thin film when the heat starts at a point and diffuses around. In its generality the case is therefore comparable, as Maxwell points out, to that of which Fourier gave the complete solution (art. 384, 'Analytical Theory of Heat,' p. 382, Freeman's translation), for the diffusion of heat in all directions, where the temperature is represented by the triple integral

$$\iiint \frac{d\alpha\, d\beta\, d\gamma}{2^3 \sqrt{\pi^3 k^3 t^3}} \cdot e^{-\frac{(\alpha-x)^2+(\beta-y)^2+(\gamma-z)^2}{4kt}} \cdot f(\alpha, \beta, \gamma),$$

in which, if we write $r=\sqrt{(\alpha-x)^2+(\beta-y)^2+(\gamma-z)^2}$, the exponential $e^{-r^2/4kt}$ will represent the value contributed to the mean temperature at the point (x, y, z) whose distance from the origin is r. In the present case of diffusion of electric currents in the plane (xy), a similarly constructed double integral may be employed to represent the distribution of vector-potential, the quantity symbolized by k (the coefficient of the intrinsic rate of diffusion) being replaced by $\frac{1}{4\pi\mu_1 C_1}$ and $\frac{1}{4\pi\mu_2 C_2}$ in the exponential.

Now, where the whole energy of the electromagnetic disturbances is thus converted in the conducting medium into the energy of currents diffused through its substance, no wave will be propagated; or, as Maxwell has shown, the substance will be opaque to light, the energy of the diffused currents being frittered away into heat within the conducting medium by reason of the resistance encountered.

17. Case iii. (*Medium possessing both Dielectric Inductive Capacity and Conductivity, the values of* K *and* C *being of comparable order of magnitude, but having different values in different directions*).

We have (from § 11) the equations

$$\left.\begin{aligned} 4\pi\mu_1 C_1 \frac{dF}{dt} + \mu_1 K_1 \frac{d^2F}{dt^2} &= \frac{d^2F}{dz^2}, \\ 4\pi\mu_2 C_2 \frac{dG}{dt} + \mu_2 K_2 \frac{d^2G}{dt^2} &= \frac{d^2G}{dz^2} \\ 4\pi\mu_3 C_3 \frac{dH}{dt} + \mu_3 K_3 \frac{d^2H}{dt^2} &= 0. \end{aligned}\right\} \quad . \quad . \quad (3\,bis)$$

F and G being the components of vector-potential in the x and y directions respectively, the problem is to determine at what rate these will be diminished by absorption in passing through a given thickness z of the medium when the conductivities per unit volume in those directions are respectively C_1 and C_2. The proportion borne by the transmitted electromagnetic displacements of the luminous wave to the original displacements, after traversing a thickness z of the crystal, will (neglecting the small proportion lost by surface reflexion) be expressed by an exponential of the form

$$e^{-pz}.$$

where p is the coefficient of absorption. This coefficient Maxwell has calculated (art. 798) for the case of isotropic conducting media, from the general fundamental equation, on the assumption that the disturbance may be expressed as a circular function of the form $\cos(nt-qz)$. Following the lines thus laid down, we will write:—

$$\left.\begin{aligned} F &= e^{-p_1 z} \cos\frac{2\pi}{\lambda_1}(V_1 t - z), \\ G &= e^{-p_2 z} \cos\frac{2\pi}{\lambda_2}(V_2 t - z), \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (9)$$

where p_1 and p_2 are coefficients of absorption in the x and y directions respectively, and where V_1 and V_2 are the two velocities of propagation (see § 13), and where λ_1 and λ_2 are the corresponding lengths of waves. Now, putting

$$\left.\begin{aligned} q_1 &= \frac{2\pi}{\lambda_1}, \\ q_2 &= \frac{2\pi}{\lambda_2}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and

$$\left.\begin{aligned} n_1 &= \frac{2\pi V_1}{\lambda_1}, \\ n_2 &= \frac{2\pi V_2}{\lambda_2}, \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (11)$$

whence

$$\left.\begin{aligned} V_1 &= \frac{n_1}{q_1}, \\ V_2 &= \frac{n_2}{q_2}, \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (12)$$

we may write equations (9) in the form

$$\left.\begin{aligned} F &= \epsilon^{-p_1 z}\cos(n_1 t - q_1 z), \\ G &= \epsilon^{-p_2 z}\cos(n_2 t - q_2 z); \end{aligned}\right\} \quad \ldots\ldots \quad (13)$$

in which case the expressions (9) will satisfy the differential equations (3), provided that

$$\left.\begin{aligned} 2p_1 q_1 &= 4\pi\mu_1 C_1 n_1, \\ 2p_2 q_2 &= 4\pi\mu_2 C_2 n_2. \end{aligned}\right\} \quad \ldots\ldots \quad (14)$$

It follows at once that the coefficients of absorption are

$$\left.\begin{aligned} p_1 &= 2\pi\mu_1 C_1 V_1, \\ p_2 &= 2\pi\mu_2 C_2 V_2. \end{aligned}\right\} \quad \ldots\ldots \quad (15)$$

Here C_1 and C_2 are volume-coefficients of conductivity, and would require to be replaced by their values l/bzR_1 and b/lzR_2 if a given rectangular plate of the substance, of length l (parallel to x), breadth b, and thickness z, were measured, and found to have resistances of R_1 and R_2 respectively in directions parallel to x and y. In the actual case of the tourmaline, however, in which no measurements of resistance have yet been made, the volume-conductivities C_1 and C_2 may stand for conductivities in general. And the proportions of the incident (unpolarized) light transmitted by the crystal will be as follow:—

Ordinary ray (polarized in a plane (xz) of principal section; electric displacements parallel to y, magnetic displacements parallel to x),

$$\text{proportion transmitted} = \epsilon^{-2p_2 z} = \epsilon^{-4\pi\mu_2 C_2 V_2 z}.$$

Extraordinary ray (polarized in a plane (yz) perpendicular

to the optic axis; electric displacements parallel to x, magnetic displacements parallel to y),

$$\text{proportion transmitted} = \epsilon^{-2p_1 z} = \epsilon^{-4\pi\mu_1 C_1 V_1 z}.$$

If O represent the intensity of the transmitted ordinary ray and E that of the transmitted extraordinary ray, we have

$$\frac{O}{E} = \frac{\epsilon^{-\mu_2 C_2 V_2}}{\epsilon^{-\mu_1 C_1 V_1}}, \quad \ldots\ldots\ldots \quad (16)$$

whence

$$\frac{\log O}{\log E} = \frac{\mu_1 C V_1}{\mu_2 C_2 V_2}. \quad \ldots\ldots \quad (17)$$

Now the ratio of V_1 to V_2 is known (§ 14), the velocity of the ordinary ray V_2 being to that of the extraordinary ray V_1 in the ratio 1·8286 to 1·8504. If, therefore, the magnetic permeability were equal both along and across the axis of the crystal, and if the electric conductivity were equal in both directions, the relative intensities of the two transmitted rays would depend only on the relative velocities; and as V_1 is greater than V_2, the ordinary ray should be more freely transmitted than the extraordinary ray, which is contrary to observation. The conductivities therefore cannot be equal in fact.

Billet's values (§ 13) for the refractive indices of tourmalines of different colours show slight differences, the colourless tourmaline being apparently a little less refringent than the coloured crystals. As in this case there was no opacity, the presumption is that both C_1 and C_2 were = 0. If the fact were confirmed by observation generally that the index of refraction is less in crystals exhibiting no coloration, we should be obliged to consider K as no longer independent of C in the general equations of electromagnetic disturbances; and V, which is taken $= (\mu K)^{-\frac{1}{2}}$, would require a more complicated formula for its complete expression.

18. If, again, either the coefficient of magnetic induction or the conductivity be greater along the axis of the crystal than across it, then the ordinary ray should be transmitted more freely than the extraordinary. This is not the fact with *any* tourmalines; it is always the ordinary ray which suffers the greater absorption.

As I understand Plücker's experiment on the diamagnetism of tourmaline (§ 7 *antè*), the crystal examined by that dis-

tinguished physicist possessed a greater magnetic inductive capacity in a direction *across* the crystallographic axis than in the direction of that axis. If this observation were also confirmed for tourmalines in general, we should have some reason to expect that crystals possessing electric conductivity, even if the conductivity were equal in all directions, should show greater absorption for the ordinary ray; for if $C_1 = C_2$, equation (15) becomes

$$\frac{\log O}{\log E} = \frac{\mu_1 V_1}{\mu_2 V_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

But μ_1 and μ_2 are so nearly equal to 1 in all cases hitherto observed, that the ratio of μ_1 to μ_2 is far less than that of V_2 to V_1; and therefore the greater opacity to the ray cannot be accounted for on the supposition that it depends on differences in the magnetic inductive capacity.

19. There appears, then, to be no other explanation of the observed opacity of coloured tourmaline crystals for rays polarized in a principal plane of section than that afforded by the hypothesis that the electric conductivity is greater in directions at right angles to the crystallographic axis than along it. One fact of some importance bearing upon this point is an observation which I have made, that the more opaque the crystal in general the greater is the inequality of absorption of the ordinary and extraordinary rays. The green tourmaline "C" in my possession, which is about 2 millim. thick, transmits both rays partially; but cuts off about three fourths of their intensity from ordinary rays, and above half their intensity from extraordinary rays. It is about 30 millim. in length, and appears to be perfectly opaque in that direction. On the other hand, a slice of a jet-black tourmaline, the property of University College, Bristol, not more than 0·2 millim. in thickness, is perfectly opaque to the ordinary ray; but it transmits extraordinary rays at about half of their intensity. Not only must the conductivity as a whole be higher in the latter case, but the ratio of the two conductivities must be higher in the latter than in the former; and the transverse conductivity must be greater than the longitudinal. The latter crystal was too small to permit of verification of these inferences by direct experiment.

III. *Electric Conductivity of Tourmaline Crystals.*

20. The conducting-power of the tourmaline for electricity is very feeble; and the only determinations that have been made of its relative conducting-powers in longitudinal and transverse directions are determinations, not of the flux of electricity through a slab or film of the substance, but of the superficial conductivity along a face of the crystal. This superficial conductivity has been examined by two slightly different processes, by de Senarmont* and by Wiedemann†.

21. De Senarmont's process consisted in covering the face of the crystal with tinfoil through which a truly circular hole had been punched. The foil was fixed over the crystal with gum or varnish, and was connected to earth. At the centre of the exposed circle a metallic point was fixed in an insulating support; and by this means the electricity stored in a Leyden jar could be made to flow across the circular space from the centre to the circumference. With powerful discharges from a Leyden battery sparks leapt along the crystal face, leaving a permanent trace along the path of least resistance. Later experiments were conducted in a partial vacuum, when the discharge took place quietly in luminous streaks of a pale-violet colour along that diameter of the circle which corresponded to best conductivity along the surface.

The crystals operated upon by de Senarmont were three black tourmalines from Greenland, in the collection of the École des Mines, having plane mirror-like faces tangential to the lateral edges of the primitive rhombohedron and slightly striated ("stries à peine sensibles"). With circles of three different sizes, de Senarmont found the maximum conductivity to lie in a direction parallel to the axis.

22. Wiedemann's process consisted in producing an electric "figure" upon the surface of the crystal, which was dusted over with powdered sulphur, or lycopodium, or red-lead, and then exposed to the discharge of electricity from a finely-pointed conductor close to the surface. The powder was repelled from the point, and heaped itself all round a clear space. In the case of equal conductivities this space was a

* *Ann. de Chim. et de Phys.* 3e série, t. xxviii. p. 257.

† Ibid. t. xxix. p. 229; and Pogg. *Ann.* lxxvi. p. 404, and lxxvii. p. 534.

circle; in the case of unequal conductivities an ellipse whose major axis indicated the greater conductivity. Wiedemann only examined one specimen of tourmaline. He states that "on the faintly striated prismatic faces of the crystal employed, the larger diameter of the electric figure shows itself parallel to the principal axis." He adds, that in the case of other optically negative crystals (including calc-spar) the electric conductivity is greater along than across the axis. (He notes *rutile* as an exception.) But he appends, as a general conclusion, that the electricity is propagated in crystals more rapidly in that direction in which the propagation of light is the more rapid; which dictum exactly contradicts his own observations on calc-spar and on tourmaline, in which the velocity of the extraordinary ray is greater than that of the ordinary ray.

23. Now, if we are to accept these observations on the superficial conduction of natural tourmaline crystals with striated faces as establishing the electric conductivity of tourmaline to be a maximum along the axis and a minimum across it, we shall have to admit that, of all substances examined, tourmaline forms the solitary exception to the rule that the thermal conductivity and the electric conductivity of substances go together *pari passu**. There is no uncertainty as to the thermal conductivity of tourmaline, its transverse conductivity being about twice as great (see § 8 *antè*) as its longitudinal conductivity.

24. Both observers stated that the faces of the crystals were *striated*. De Senarmont appeared, indeed, to think that natural striation interfered less with the regularity of conduction than the invisible striations of an artificially polished face†. I am inclined to think from my own observations that, on the con-

* See Tait, Trans. Roy. Soc. Edinb. 1878, where, however, it appears that German silver, while superior in thermal conductivity to lead, is inferior to that metal in electric conductivity, being the single known exception to Forbes's rule.

† "Quant aux stries et aux aspérités naturelles, elles ne semblent pas avoir une influence appréciable tant qu'elles ne sont pas extrêmement prononcées. J'ai donc autant que possible, pour être sûr des résultats, cherché à opérer sur des faces naturelles ou obtenus par le clivage." *Loc. cit.* p. 264.

trary, the natural striations of the crystal greatly affect the conditions of surface-conductivity. I have repeated both methods of experiment upon tourmalines with natural and with artificially-cut faces. In the former case, the crystals tried were black striated crystals from Norway. They showed, as did the crystals used by de Senarmont and by Wiedemann, a longitudinal conductivity higher than the transverse conductivity. I cleaned one of these crystals, first with hydrochloric acid, and then by rubbing its surface in boiling paraffin. When cold it was carefully cleaned with a piece of dry leather, and the experiments were repeated. De Senarmont's method now showed a transverse conductivity, while Wiedemann's method gave an indecisive result.

25. I therefore tried another method, as follows :—A small circular drop of pure olive-oil was deposited upon the middle of the face of the crystal. A pointed needle held in a non-conducting support was fixed centrally above it, and then the knob of a charged Leyden jar was cautiously approached. The oil-drop spread out somewhat irregularly across the surface; and at its centre appeared a clear space from which the oil was repelled. This clear space was distinctly elliptical, the major axis of the ellipse being transversely placed across the axis of the crystal. The natural striations, however, rendered the form irregular. When the artificially-cut green tourmaline ("C") mentioned in § 19 was employed, the elliptical space in the centre of the oil-drop was much more satisfactorily observed. The ratio of the minor axis to the major axis was not greater than 1 : 2.

It is greatly to be wished that some more exact and more reliable measurements were made of the conductivity of tourmaline in the two principal directions along the axis and across it. Although these more reliable measurements are still wanting, I am disposed to think that my own experiments, backed by the analogy of the thermal conductivity (about which there is no uncertainty whatever), are sufficient to establish qualitatively that the electric conductivity of tourmaline is greater in directions at right angles to the axis than in the direction of the axis. If this be established, the theory of opacity advanced above is proved.

26. There is, indeed, one other possible way of accounting

for opacity in a homogeneous medium besides the supposition made above, that the medium should possess electric conductivity of one kind or another. This alternative way of explaining opacity supposes that a luminous oscillation may pass into a calorific one of the same period. The vibrations of light being regarded as due to rapid alternations in vector-potential, the particles of a medium transmitting the luminous waves must be subjected to alternately directed electromotive forces. Now let there be in the medium a particle of matter whose natural period of oscillation coincides with that of the wave. This particle will be subjected to alternate inductions which will displace electricity in it from side to side, the (electro-) kinetic energy of the movement changing to (electro-) potential energy and back again to the kinetic form at each half swing, as in the alternations of the swinging pendulum. There is no difficulty in understanding that, under this action, the mass of the molecule will be set swinging. It is easy to set a pendulum, consisting of a metal ball hanging by a silk thread, into vibration by subjecting it to periodic electric inductions whose period agrees with that of the pendulum. Thus the (electro-)kinetic energy of the wave passes over into the (pondero-)kinetic energy of the oscillating particle; which is merely another way of saying that the light is absorbed and changed into heat. This action, however, can only account for absorption on the assumption that the medium is homogeneous, and its individual particles themselves conductors. But if the medium be homogeneous, all its particles will have similar periods of oscillation. This hypothesis may therefore account for selective absorption in media, though it is not adequate to explain general absorption. If the medium be not homogeneous, a *third* explanation of opacity is possible. In a *non-homogeneous* medium there is no need to suppose conductivity to exist; for heterogeneity of structure affords in itself a possible explanation of electric absorption; and if electric absorption were possible in the medium, the variations of vector-potential would no longer be propagated without loss through the medium, any more than they can be through a medium possessing true conductivity. And if, by reason of structural differences in different directions (differences of fibre, lamination, cleavage, and the like), the degree of electric

absorption were different in different directions, then such a medium might possess also a directed opacity. But such an opacity would be limited by the limitations of electric absorption in general, and would probably be quite distinguishable from the opacity arising from conduction in the medium. Were electric absorption possible, we could no longer omit functions of ψ, the (scalar) electric potential, from the general equations of electromagnetic disturbances assumed in § 10 and in the succeeding development of the theory.

27. The main argument for rejecting the supposition that electric absorption can account for opacity is derived from the consideration that such a medium, after having absorbed charges of opposed signs at different surfaces of its heterogeneous structure, would, when left to itself, slowly recover; and would give rise to phenomena of recovery, variations of vector-potential taking place in the medium in inverse order after the lapse of time. Whether this action may furnish a possible explanation of the phenomena of phosphorescence (*Nachleuchtung*), is a suggestion which may be worth future consideration. Whether the optical properties of tourmaline are to be regarded as dependent on its conductivity or on any other physical property, the physical property on which they depend is certainly a directed property; and its action is such that the crystal possesses what Maxwell called "electric elasticity" in a longitudinal and not in a transverse direction. Now, as those bodies which possess "electric elasticity" are observed for the most part to phosphoresce under the impact of electrified molecules in the negative glow produced in very attenuated vacua such as Crookes has obtained, whilst those bodies which do not possess this property do not phosphoresce under the same circumstances, I venture to predict that, if a slice of tourmaline cut parallel to the axis be found to phosphoresce at all when exposed to the negative discharge, its phosphorescence will be found to consist chiefly of rays polarized in a plane at right angles to the axis—or, in other words, that it will emit the same kind of rays as it transmits. Whether this prediction be verified or not, however, does not affect the validity of the theory of opacity of tourmaline crystals here advanced.

June 4, 1881.

XXXI. *Electrostatic Investigations, especially relating to the Division of Induction in the Differential Inductometer and in the Electrophorus.* By Dr. James Moser.

The Differential Inductometer.

In the year 1838 Faraday completed his experiments on Specific Inductive Capacity, thus virtually repeating the investigations of Cavendish, published some sixty years before. At the end of his communication Faraday gave a description of an apparatus, the "Differential Inductometer," for the determination of such inductive capacity.

This serves as the point of departure for the following investigation; but I shall first, and chiefly, consider the electrostatic induction in a single medium, namely the atmospheric air; so that the question of "specific induction," a question involving more than one medium, will be considered later.

Faraday, in his 'Experimental Researches' (§ 1307), describes the above-mentioned apparatus as follows:—"Three circular brass plates about five inches in diameter were mounted side by side upon insulating pillars. The middle one 'A' was a fixture; but the outer plates 'B' and 'C' were moveable on slides, so that all three could be brought with their sides almost into contact or separated to any required distance. Two gold leaves were suspended in a glass jar from insulated wires. One of the outer plates, 'B,' was connected with one of the gold leaves, and the other outer plate with the other gold leaf. The outer plates B and C were adjusted at the distance of an inch and a quarter from the middle plate 'A'; and the gold leaves were fixed at two inches apart. 'A' was then slightly charged with electricity, and the plates 'B' and 'C' with their gold leaves thrown out of insulation *at the same time*, and then left insulated. In this state of things 'A' was charged positive inductrically, and B and C negative inducteously; the same dielectric (air) being in the two intervals, and the gold leaves hanging, of course, parallel to each other in a relatively unelectrified state."

Faraday affected the relation of the induction from A to B to the induction from A to C by the introduction of various

dielectrics. I vary such relationship by altering the distance between B and C from A.

Faraday brought a plate of shellac between the middle plate A and one of the outer plates, B. Thereupon the gold leaves approached one another. The leaves again separated when the shellac was taken away. According to Faraday, the attraction is due to the increased induction where the shellac is, causing A to induce more negative electricity on B. The side therefore of B (and its gold leaf) furthest from A becomes positive. On the other outer plate C there is less negative electricity induced; and the outer side of this plate, together with the gold leaf connected with it, becomes therefore negative. Hence the gold leaves attract one another.

In my experiments I employed three zinc plates of 30 millim. diameter, and made use of, on some occasions, a glass jar (described above) having the two insulated gold leaves. Sometimes, however, I used two electroscopes, one of which was connected with the one and the other with the other outer plate. Under these conditions the kind of electricity which was to be found on the plate was easily determined.

I should like to be allowed to mention a few details which I think are of interest in electrostatic investigations. The insulation of the wire to which the gold leaves were hung was effected simply by passing the wire through a tube of ebonite having an external diameter of 5 millim. and 1 millim. opening.

In order to avoid binding-screws, the numerous edges of which are troublesome in electrostatic experiments, connexions were made by boring conical holes of diameters from $\frac{3}{4}$ tapering to $\frac{1}{2}$ millim., and simply thrusting the wires into the holes. No electricity must be allowed to settle on the glass of the electroscope. I therefore employed an ordinary cylindrical glass 15 centim. high and 10 centim. wide, but led round the glass, inside and outside, a continuous strip of tinfoil 3 centim. wide, parallel to the gold leaves and connected with the earth. By this means the electricity of the leaves induced electricity of the opposite kind in the tinfoil; and if this charge became too strong, the leaves touched the tinfoil and discharged themselves. The glass was provided with a wooden cover, through which passed the little ebonite tube

enclosing the wire. Each zinc plate was fastened to a horizontal Z made of shellac. The three Z's overlapped one another, so that the plates could be brought to within 1·5 centim. of one another.

Division of Induction.

The three plates of the differential inductometer are to be looked on as two condensers which have one plate, namely the collecting-plate, in common. From this plate, as "inductric," the induction begins, and ends on the two side plates as "inducteous." In this arrangement the division of the induction corresponds to the division of the current in flowing electricity.

But before I proceed further with the physical considerations, which would appear hypothetical, I shall deduce the mathematical from the theory of potential.

If we look upon the differential inductometer as formed of two condensers, the total electricity, E, on the middle plate consists of two parts, e_1 and e_2;

$$E = e_1 + e_2 \quad \ldots\ldots\ldots (1)$$

so that e_1 is the charge on one plate, and e_2 on the other. The value of each of these is found in the following manner. According to Green*, if e be the charge on a plane condenser whose plates have the surface S and the distance r, and if the potential-function on the one is V, while the other is connected with the earth, then

$$e = \frac{VS}{4\pi r}.$$

In the derivation of this equation it is assumed that r is small in comparison with the diameter of the plates, an assumption to which I will return afterwards.

We will apply this formula to the two condensers of the differential inductometer. All three plates have the same surface S. The middle one has the potential V; the two outer ones are connected with the earth. Let the distance of the plate of which the charge is e_1 be r_1, that of the one with charge e_2 be r_2. Then

$$e_1 = \frac{VS}{4\pi r_1},$$

* Green, Essay, § 8; Thomson, Papers, § 53.

and

$$e_2=\frac{VS}{4\pi r_2},$$

and, accordingly,

$$e_1 : e_2=\frac{1}{r_1} : \frac{1}{r_2}. \quad \ldots\ldots\ldots (2)$$

In other words, the charges are inversely proportional to the distances. The values of the two charges are derived immediately from equations (1) and (2). According to these,

$$e_1=\frac{r_2}{r_1+r_2}E \quad \ldots\ldots\ldots (3)$$

$$e_2=\frac{r_1}{r_1+r_2}E. \quad \ldots\ldots\ldots (4)$$

These formulæ, which are the same as those for the divided current, are only absolutely true for plates of an infinite size. They signify that the inductive capacities of the two condensers which form the differential inductometer are inversely proportional to the distances of the plates. If we use the term "inductive resistance" to denote the reciprocal of the inductive capacity in the same way as conductivity is the reciprocal of resistance, then, in the case of infinite plates, the inductive resistance is directly proportional to the distance. In such a case of infinite plates the equipotential surfaces are planes parallel to the plates, and the tubes of force are cylinders at right angles to them.

This electrostatic condition is converted into the corresponding electrodynamic one if a conducting liquid is placed between the plates. If, then, the plates are kept at the same electrical level by (say) a battery, then a divided current would pass from the middle plate through the liquid to the two side plates; so that the middle plate would be an anode, and the side plates kathodes; and the division would then take place in such a manner that the strength of the two branch currents would be inversely proportional to the respective resistances; or, since the latter are proportional to the distances, the currents would be inversely as the distances*. Just as we incur an error when we pass from the law that the divisions of the current are inversely proportional to the

* See Currents between Plates, Wied. *Galv.* § 116.

distances in the case of infinitely large plates, to the case where the plates are simply very large, so we incur a similar error in electrostatics when we apply the formula for infinitely great plates to the inductometer.

The case in electrodynamics which corresponds to the nductometer (which we regard as an apparatus for the livision of induction) would be the branching of the current etween three round plates. If we imagine the differential nductometer to be plunged into a conducting liquid and the otentials to be constantly maintained, then a current would ass from the middle plate as anode to the external plates as athodes. Further, if in both cases we construct the system f the surfaces of equal potential, then, if their equation be

$$V = \text{constant},$$

V in both cases (that is, by the branching of the current and in the inductometer) would satisfy the same differential equation, and the same limiting conditions must be fulfilled. We should get in both cases the same system of surfaces of electrical level; and the perpendiculars to these surfaces would have in the one case to be regarded as lines of force, and in the other as lines of flow. The greater the plates are, the more nearly flat are the surfaces of electric level, and the straighter are the lines of force.

Induction and conduction act, therefore, in the same lines. If, in order to fix our ideas, we take spermaceti as an intervening plate, as Faraday did, we find, with him, "spermaceti to be a dielectric, through which induction can take place" (Exp. Res. § 1322). But "spermaceti is also a conductor, though in so low a degree that we can trace the process of conduction, as it were, step by step through the mass. . . . . Here induction appears to be a necessary preliminary to conduction" (§ 1323). And although Faraday could not, as we have done, formularize the division of the induction in the same way as the branching of the current is formularized, still he had this agreement in his mind. That he could not formulate this idea was the reason why he was misunderstood; and this is the reason which has induced me to examine the point more carefully.

In one case of electrostatic induction through the air Faraday replaced a part of the air by sulphur, and found

that the induction was now greater than when the air was there which the sulphur had replaced.

He now compares this case with that of the branching of a current in bad conductors, one of which he replaced by a good conducting wire. Then a stronger current would flow through the wire than flowed through the bad conductor which it had replaced. And as much less electricity would flow through the remaining bad conductors as more through the wire.

This is the meaning of Faraday's words, "Amongst insulating dielectrics some lead away the lines of force from others as the wire will do from worse conductors" (§ 1331).

I shall, in the following, consider some of the applications of this conception of the inductometer as a dividing of electrostatic induction.

Method for Determining Inductive Capacity.

The methods for determining electrical resistance which are based upon division of the current may be transferred to the measurement of inductive capacity. In Wheatstone's bridge, for example, first given by Christie, we determine an unknown resistance as a fourth proportion to three known resistances. For this purpose, the current between a point of higher and a point of lower potential is divided. Two points, one on each of the branches, are found having equal potential. They divide, therefore, the resistances of the two branches in like ratio. Then no current passes round a galvanometer introduced between these points. In the differential inductometer the beginning of the branching is the middle inductric plate, whose electric level is V, and the end of the branching is on the two inducteous plates, where the potential is zero. Between the inductric plate and each of the inducteous plates let us now introduce a metal intermediate plate of equal potential, so that there are four divisions whose inductive capacities are proportional to one another in pairs. If the inductive capacity of one of these divisions is altered by introducing another dielectric than air, then the capacity of the other division must also be altered, in order to restore the original proportion. The capacity of this second division is changed by altering the distance between its limiting plates until the original

equality of the electrical potential of the two middle plates is again reached. This is recognized by finding that a quadrant electrometer connecting the two shows no deviation. Thus the measurement of inductive capacity is reduced to measuring a length. This method is essentially the same as that recommended by Maxwell and Sir W. Thomson to Mr. Gordon for his measurements of inductive capacity, published a year ago (Phil. Trans.).

Theory of the Electrophorus.

A further instance of the branching of induction is found in the electrophorus. Being about to deduce its theory and to discuss the number of electrically effective layers, I shall start from Faraday's differential inductometer. Such a theory of the electrophorus as takes Faraday's views into account has not yet been given. Faraday has not developed it; and the question as to how many layers are electrically effective is not treated by Maxwell, who views the electrophorus not as a symmetrical construction consisting of a plate of ebonite with two movable metallic coverings, but as an unsymmetrical arrangement consisting of a single ebonite plate covered at the back with metal, and having only one movable metal plate.

In this special manner we shall obtain a theory of the electrophorus, and get a fixed point from which to view the different theories based on electrical action at a distance and expressed in the language of the influence theory. We shall approach nearest to that one of these theories which has lately been supported by Herr v. Bezold (Pogg. *Ann.* cxliii.).

The electrophorus, as I view it, is symmetrical. It is a non-conducting plate with two movable coverings, and can thus be used as a Franklin's disk, a Leyden jar, or a condenser. My electrophorus consisted of a circular ebonite plate 1·5 millim. thick and 30 centim. diameter. The coverings were of zinc and were of the same diameter, one of them being provided with an ebonite handle. For other purposes I used three plates of the same shape, of thinner ebonite, together with other plates of zinc of similar dimensions.

The simplest supposition is that the ebonite plate, lying on the one uninsulated metal covering, being beaten by the

fox's tail becomes negatively electric. Then induction starts from this negative layer of this ebonite plate as inductric layer (*inductor*). The inducteous layer (*inducendus*), where the induction ends, is the underlying uninsulated metal plate. After putting on and uninsulating the upper metal plate, however, the induction branches off again from the upper negative layer of the ebonite plate as inductric body (*inductor*), and extends to both the metal plates as inducteous bodies (*inducendus*). If there exists, as we have supposed, only one inductric layer in the electrophorus, namely the negative one on the upper surface of the ebonite plate, the differential inductometer could be viewed as a scheme of the electrophorus. The negative layer of the electrophorus would be represented by the negatively charged middle inductric plate of the differential inductometer; and the two metal coverings of the one apparatus would correspond to the two of the other. Further, this similarity of the two apparatus appears still more complete if we use the differential inductometer as electrophorus for producing electricity. We can uninsulate the one plate of the differential inductometer; and bringing the other near, we can draw out of it a negative spark; then withdrawing it, we can get a positive spark. But one difference now presents itself, and proves the insufficiency of our last scheme. As to the differential inductometer, it is perfectly indifferent whether we uninsulate the right outer plate and insulate and discharge the left one, or if we uninsulate this and change the distance of the right one. We always get positive discharge from that outer plate which we have removed from the negative middle plate. The same kind, namely positive discharge, after removal, must take place if there existed only one inductric layer. Then there is, as Faraday (§ 1255) has already pointed out, no difference as to the kind of induction through air and that through ebonite. Therefore, the ebonite plate being inverted, the upper metal covering (which is now, however, lying on the unrubbed ebonite surface) must give positive electricity when it is lifted, as the plate did before.

This, however, is not the case. If we turn the ebonite plate over, the upper metal covering, on being lifted off, gives negative electricity, while formerly it gave positive.

The differential inductometer, which gave positive in both cases, is therefore not a sufficiently accurate scheme to explain why we get,

(1) when the rubbed surface is above, a + spark,

(2) when the rubbed surface is below, a — spark, from the lifted metal.

The simplest completion of the differential inductometer having only one inductor plate, to make a scheme of the electrophorus, is effected by adding a second inductor plate (a positively charged one), which corresponds with the underside of the ebonite plate. In fact, after beating, the ebonite plate attaches itself so closely to the metal sole, that I could hold the sole vertical without the ebonite plate sliding down. At first the negative layer of the rubbed surface induced positive electricity in the metallic sole. The induction is followed by conduction and discharge; a part of the positive electricity goes over from the sole to the lower side of the ebonite plate. On the other side the negative electricity penetrates deeper from the upper surface into the ebonite; so that there are two layers on the ebonite plate—a negative one on the upper side, a positive one on the lower side. For the understanding of the question, it is here sufficient to regard these layers as plane, without discussing the question of the thickness.

With the help of these two layers we have to explain the two observations:—

(1) The + spark when the metal plate is lifted from the rubbed surface;

(2) The — spark when it is lifted from the unrubbed one.

For the proof of this theory we shall deduce further consequences from it; and we shall have to confirm these by experiment. The complete scheme of the electrophorus consists of four plates:—

(1) One negatively charged;

(2) One positively charged.

These two are as inductric bodies.

(3 and 4) Both metal coverings as inducteous bodies (*inducendus*).

To be brief, we will call the covering on the rubbed negative surface of the ebonite plate "cover;" that on the other, positive,

unrubbed side, "sole;" so that we have in succession

cover,
negative layer,
positive layer,
sole.

Let us call b the distance of the sole from the positive surface, and d the distance of the cover from the negative layer.

If c is the thickness of the ebonite plate, a layer of air thinner in the ratio of the inductive capacity of the ebonite (2·2) would correspond to it, *i. e.* of the thickness

$$c' = \frac{c}{2 \cdot 2};$$

so that in our scheme the four metal plates would stand at the distances

$$b, \quad c', \quad d.$$

The rubbed side may contain the quantity of electricity

$$-\mathrm{E};$$

and from the sole the part

$$+\alpha\mathrm{E}$$

of the induced quantity may have passed on the unrubbed surface:

$$\underset{\text{Sole.}}{|} \; b \; \underset{+\alpha\text{E.}}{|} \; c' \; \underset{-\text{E.}}{|} \; d \; \underset{\text{Cover.}}{|}.$$

Then, according to the equations (1), (3), and (4), the quantity $-\mathrm{E}$ induces a total amount of $+\mathrm{E}$, viz.:—

In the sole.	In the cover.
$\frac{+d}{b+c'+d}\mathrm{E}.$	$\frac{+b+c'}{b+c'+d}\mathrm{E}.$

In the same manner the quantity of the lower side $+\alpha\mathrm{E}$ induces a total of $-\alpha\mathrm{E}$, viz.:—

In the sole.	In the cover.
$\frac{-\alpha c'-\alpha d}{b+c'+d}\mathrm{E}.$	$\frac{-\alpha b}{b+c'+d}\mathrm{E}.$

So that all together is induced:—

In the sole.	In the cover.
$\frac{+d-\alpha c'-\alpha d}{b+c'+d}$	$\frac{+b+c'-\alpha b}{b+c'+d}\mathrm{E}.$

The numerator of the electric quantity in the cover

$$+b+c'-\alpha b$$

is always positive. That is, there is always induced in the metallic covering on the side of the rubbed surface positive electricity; and we get, on removing the plate, a positive spark.

On the other hand, we recognize that the numerator of the electric quantity in the sole

$$+d-\alpha d'-\alpha d=d(1-\alpha)-\alpha d',$$

$\alpha d'$ being constant, changes its sign when d increases: viz. d (that is, the distance of the cover) being small, negative electricity is induced in the sole, and we get, on lifting the sole, a negative discharge. This distance d, however, is small, almost nothing, if we invert the ebonite plate and lay it with its rubbed surface close to the metal plate. Then we get from the upper metal plate (the sole), on lifting it, a negative discharge. Thus the two phenomena which we intended to explain, (1) positive discharge in the original position, (2) negative discharge in the inverted position, of the ebonite plate, are deduced from our theory.

The electrophorus contains, therefore, two inductric layers—one negative, on the upper side, one positive, on the lower side of the ebonite plate.

Experiments with the Electrophorus.

If the theory developed by us is true, the consequence which we are about to draw now must be confirmed by experiment. According to the last formula for the numerator of the electric quantity of the sole, positive electricity must be induced in the sole when the distance d of the rubbed surface from the cover is increased, so that we get

$$d.(1-\alpha)>\alpha d'.$$

This happens indeed, as we see, if we lay the inverted ebonite plate, not immediately on the cover, but place it insulated some height above the cover, as Herr von Bezold has done already. Now the other plate, the sole, being laid on the unrubbed surface, uninsulated and lifted, gives a positive spark. Whilst the sign of the electricity of the cover (the plate on the side of the rubbed surface) is always positive, the sign of the electricity of the sole (the plate on the side of the unrubbed surface) changes. It is positive when the distance of the other metal plate (the cover) from the rubbed layer is small; on the contrary, it is negative when this distance is great.

In other words, when the cover is on the side of the stronger negative inductric layer, the induction of the latter always prevails; in it positive electricity is induced.

In the sole, however, the nearer but weaker positive layer induces negative electricity. To this there is to be added the positive electricity induced by the stronger but more distant negative inductric layer. The more distant the cover is, the more positive electricity is induced in the sole; so that, the distance of the cover being large, more positive than negative electricity can be induced.

On the two sides of the ebonite plate the sign of the discharge is differently affected.

1. The ebonite plate lying close to the metal plate, the other, lifted, metal plate gives:—

(*a*) The rubbed surface being above, a positive discharge;

(*b*) The unrubbed surface being above, a negative discharge.

2. The ebonite plate lying some height above the metal plate, we get, on the contrary, quite indifferently, whether (*a*) the rubbed surface is above, or (*b*) the unrubbed surface, in both cases positive discharges.

Thus we have the means of recognizing not only—

(1) on which side an ebonite plate is charged positively,

(2) on which side it is charged negatively, but also

(3) if it had been charged originally negatively on the one side or

(4) positively on the other side.

For this purpose we place the ebonite plate to be tested close to an uninsulated metal plate. Then we put a second metal plate on the ebonite disk, uninsulate it, and try the electricity induced in it; the opposite one exists in the upper surface of the ebonite plate.

The ebonite plate is now inverted, put again close to the uninsulated metal plate, and the kind of electricity of the other surface of the ebonite plate is determined in the same manner. Thereby we learn which kind of electricity exists in each surface.

Now the ebonite plate is tested at some height over the metal plate, at first in the original, then in the inverted position; it is, however, to be lifted so high that in both cases the same kind of electricity is induced. Then the plate contains

a surplus of the opposite kind, and has been charged with it originally on that side on which according to our trial it exists.

Adding the two quantities of electricity which we have found induced in the sole and in the cover, we get, in accordance with our supposition,

$$-E(1-\alpha).$$

The greater the quantity which is induced in the cover, the less is induced in the sole, and *vice versâ*. If we join the cover with one electroscope and the sole with another, both electroscopes show a divergence on moving one of the plates, but in opposite senses.

Through a conducting wire from the cover to the sole there flows a current on moving one of the plates; so that the quantity which flows to the sole has left the cover; whilst in the electrophorus itself between sole and cover (*i. e.* in the remaining part of the circuit) changes of induction take place. In the ordinary experiments with the electrophorus this conducting wire is represented by the earth, the base being uninsulated. Here we can speak of a circuit only with the same right as in the case of a telegraphic battery with earth-conduction. If the conduction is broken by insulating the sole after having it uninsulated, the electrophorus is without effect. As to the changes of induction in the interior of the electrophorus (which we may imagine as a polarization of the dielectric), I will further adduce the following experiments:—

If the ebonite plate, put on the uninsulated base, is strongly excited, it attaches itself to the base. If now the cover is put on and both metal plates are uninsulated at the same time, it attaches itself to the cover, so that we can lift the plate by means of the cover. A current of positive electricity has flowed at the moment of uninsulating from the sole through the outer conducting wire to the cover. Before the current has flowed, the induction (polarization) went wholly through the ebonite plate; after the current the inductive (polarizing) effect of the excited layer extends, for the greater part, through the thinner interval of air to the cover, and only for a smaller part of it through the thicker ebonite plate to the sole.

Finally, I may mention an experiment in which branching of induction, as well as branching of conduction, may easily

be observed. I beat the ebonite plate lying on the uninsulated base, and put on the excited surface of the first another equal, but not excited, ebonite plate, and then on this the metal cover. This cover, being uninsulated and lifted, gave positive sparks, just as if there had been in place of the upper ebonite plate a corresponding layer of air. Immediately after this I tried the upper ebonite plate, endeavouring to use it alone as the disk of an electrophorus. But this trial did not succeed; the plate was ineffective.

Now I repeated the experiment, laid the same plate again on the rubbed surface of the first ebonite plate, put on it also again the cover, but left the apparatus unaltered during twelve hours. In this case there is ebonite on the two sides of the inductric layer of the ebonite plate; induction extends from this layer through ebonite to the sole and to the cover. In the same manner the conduction—the penetration or absorption of electricity—must take place to both sides; and I expected that the negative electricity would penetrate not only into the lower ebonite plate, but would go over to the upper plate also. This is indeed what took place. After twelve hours the upper plate could be used as the disk of an electrophorus. Both plates gave now strong and, as it seemed, equal effects. As was to be supposed, the upper plate was negatively charged on its lower surface, with which it lay on the inductric layer, and had therefore to be inverted in order to give similar discharges to those of the first plate.

If we fix our attention specially on the upper ebonite plate, we find:—

(1) That the effect of *induction* through it began almost instantaneously (for immediately after having laid this upper plate on the excited lower one I could put on, lift, and discharge the cover); and that this effect of induction had disappeared also almost instantaneously when I tried to use the plate alone for the electrophorus.

But, further, we have seen (2) that slowly another *inherent* change took place: a penetration of electricity occurred which made the plate more duringly effective as an electrophorus-disk.

XXXII. *On a Wave-apparatus for Lecture-Purposes to illustrate* Fresnel's *Conception of Polarized Light.* *By* C. J. Woodward, *B.Sc.*

[Plate XIV.]

In the ordinary apparatus for illustrating a plane wave, a series of cranks or eccentrics are attached to one axle, the successive cranks or eccentrics being turned through small, but equal angles. Attached to the cranks or eccentrics are rods, each of which is terminated by a ball, to represent one of the particles of the wave. On turning the axle each ball rises and falls in succession, producing a plane wave. This apparatus is known as that of Powell.

The arrangement I am about to describe consists of two such apparatus, with the rods connected together at right angles to each other. The axles of the apparatus are linked by a rod so that they turn together; and, finally, an adjustment allows the cranks to be placed relatively to each other in any desired position.

The apparatus, divested of supports and accessories, is shown in the figure, drawn in isometric perspective. The cranks 6, 5, 4, 3, &c. turn with the axle X. The cranks are placed successively at 30° angular distance, corresponding in position to the figures on a clock-dial; and as there are twelve cranks, one complete wave is represented by a single turn of the axle.

On the axle X′ is arranged a precisely similar set of cranks. Around each crank is put a metal strap connected with a light wooden rod. These rods, a, b, c, &c., a', b', c', &c., are now connected in pairs at their free ends each by a pin; so that each pair now resembles a pair of compasses with the legs at right angles to each other. Around each pin is loosely wrapped a wire having a bullet-cast at one end; and to the other end of the wire, which, from the action of the bullet, projects vertically above the rods, is attached a pearl bead. When each pair of rods has been thus treated, we have a row of beads representing the ætherial molecules composing one wave.

To the axle X is fastened a metal disk, D, to which is attached near the edge a pin, p, surrounded by the loose

handle, H. On the axle X′ is a similar disk, but in which eight holes are drilled at 45° from each other. The holes are all tapped, that the pin p', surrounded by the handle H′, may screw into any one of them as desired. A rod, R, connects the two pins p and p', so that both axles can be turned together.

To describe the action of the apparatus, it should be premised that the starting-point of each crank is when the crank and rod are in the same straight line. Thus, regarding for the moment the first left-hand crank only, it will be at the starting-point, or zero, when the crank 6 has moved on 45° to the left. Similarly with the first right-hand crank, it will be at zero if moved back through 45° to the right; so that, in the position shown in the figure, the left-hand crank has moved through seven eighths of a revolution, while the right-hand crank has moved through one eighth; or the difference of their phases is six eighths, or three quarters; and on turning the cranks, a wave corresponding to circularly-polarized light is produced, each bead describing a circle in succession. Bring now the cranks into the position of the figure, unscrew the pin p', and, keeping the left-hand crank steady, move the right-hand crank to the vertical position upward. Now the left-hand crank, as before, has made seven eighths of a revolution, but the right-hand crank five eighths, *i. e.* a difference of phase of one quarter. On inserting the pin p' and now turning the cranks, the beads will describe the same wave as before. Now keep the left-hand crank in its first position (the position in the figure), remove the pin p', and turn the right-hand crank until it is at 45° from the vertical below and to the left. The left-hand crank, as before, has made seven eighths of a revolution, the right-hand one two eighths, or there is a difference of phase of five eighths; and on now inserting the pin and turning the cranks, the wave produced corresponds to an elliptically-polarized ray. Of course, if the difference of phase be made one eighth or any odd number of eighths, the same kind of wave is formed. Again remove the pin, keep the left-hand crank in its first position, and turn the right-hand crank to 45° above the horizontal and to the right. Insert the pin; and on turning the cranks a plane *vertical* wave will be produced, the cranks being in similar positions, each starting at seven eighths of its revolution. Finally, adjust the

right-hand crank till the difference of phase is half a revolution, when a plane *horizontal* wave will be produced on turning the cranks.

I take the opportunity of acknowledging the assistance of my pupil, Mr. William Hall, who made several parts of the apparatus in a simple and ingenious manner.

XXXIII. *On the "Rotational Coefficient" in Nickel and Cobalt.*

By E. H. HALL, *Ph.D., late Assistant in Physics in the Johns Hopkins University, Baltimore**.

THIS article may be considered as the continuation of one published in the 'Philosophical Magazine' for November 1880, under the title "On the new Action of Magnetism on a Permanent Electric Current," in which were given the results of some quantitative investigations of a certain phenomenon recently discovered in the Physical Laboratory of the Johns Hopkins University. It will perhaps be remembered that the essential feature of this phenomenon is the setting up, in a conductor bearing an electric current, of an electromotive force at right angles to the primary electromotive force, when the said conductor is subjected to the action of a magnetic force at right angles to the direction of the current.

In the article alluded to, results were given as obtained with gold, silver, tin, platinum, iron, and nickel. The magnitude of the effect observed, relatively to the strength of the primary current, the intensity of the magnetic field, and the dimensions of the conductor, had not been determined with any accuracy in the case of nickel and tin, though it was known to be comparatively large in nickel and small in tin. The other metals ranged themselves, as regards the numerical magnitude of the effect exhibited, in the following order, viz. iron, silver, gold, platinum—the effect observed in iron being several times greater, and that in platinum several times less, than the effect in gold or silver. The fact of greatest interest, however, was that, if we called the direction of the transverse

* Read May 28, 1881.

effect in iron +, that in the diamagnetic metals, *and in nickel and platinum also*, would be −*.

In view of this remarkable disagreement in behaviour between the two strongly magnetic metals iron and nickel, it seemed highly desirable to make a quantitative investigation of the effect in nickel as soon as possible, and extend the examination to the other strongly magnetic metal cobalt. Most of the experiments to be described in this article relate, therefore, to nickel and cobalt. The examination of the latter was a hasty one, and may well be described first.

No thin strips of the metal being at hand, a slice was sawn from a small block of moderately pure cast cobalt and worked into the form of a cross. To the extremity of each arm of this cross was soldered a thin strip of copper 2 or 3 centim. long, for the purpose of making the electrical connexions. The cross of cobalt with the copper strips attached was now fastened with hard cement to a strip of glass and worked down with a file to sufficient thinness. Before placing the cross upon the glass its thickness, and that of the glass also, was measured by the calipers. After cementing the two together, the total thickness was found, and, again, the thickness of the whole after the cross had been filed down. The thickness of the cross in its final condition was thus estimated at ·45 millim., to which value an uncertainty of perhaps 10 or 15 per cent. attaches.

With this apparatus it was found that the direction of the transverse effect in cobalt is +, *i. e.* the same as that in iron. As to the magnitude of the effect, $\frac{M \times V}{E'}$ was found to be 44×10^{10}, placing cobalt between silver and iron. The specimen of cobalt used, however, contained some nickel (how much is not known accurately); and this doubtless counteracted in part the effect of the cobalt. It seems probable, however, that, allowing for all errors, the transverse effect in

* These signs are given to avoid tedious repetitions. I have here called the effect in iron + simply because its direction in this metal is that which the conductor itself bearing the current would follow, if free to move across the lines of magnetic force under the action of the ordinary "ponderomotive" force. No significance further than this is at present attached to this choice of signs.

cobalt is less than that in iron, other things being equal. The magnetic field used was about 9000 (cm.-gr.-sec.), stronger than has yet been used with iron.

We now return to the consideration of nickel.

The original experiment with this metal had been made with a specimen so irregular, that it had not been possible to determine the magnitude of the transverse effect except in the most general way. The direction had been determined beyond question. The specimen of nickel now employed, and with which the results to be given were obtained, was quite different in appearance and physical condition from the first specimen—though it was obtained in about the same manner, viz. by stripping off a piece of nickel plating from the metal upon which it had been electrolytically deposited. The first specimen was very brittle, the second quite tough. The latter was about ·001 centim. thick. As to its purity hardly any thing is known except what is told by its physical characteristics. It is probably affected by all the impurities of ordinary nickel plating. It contains very likely a little cobalt, and perhaps a trace of iron. I understand, moreover, from Professor Wolcott Gibbs, that nickel plating deposited in the usual manner (*i. e.* from an ammoniacal solution) is much affected in its physical properties by nitrogen in some way retained by the metal. It would have been desirable, of course, in all cases to work with pure metals; but such were not at hand, or easily obtainable in the proper form, and it was not thought best to defer the experiments until pure specimens could be obtained*.

The second specimen of nickel showed an effect of the same sign as the first, and numerically greater than the effect which had been observed in the specimens of iron and cobalt used.

It now became a matter of great interest to determine whether the transverse effect had really any connexion with

* This may strike some readers as unwise. It has even been suggested that the difference in behaviour of iron and nickel may be due to impurities in one or the other. This suggestion implies that the transverse effect in these metals is so related to the magnetic properties that, as they resemble each other in one respect, they should also in the other, but at the same time admits that slight impurities, such as would certainly be very far from reversing the magnetic property of either metal, may reverse the transverse effect in the same. This does not seem probable.

the magnetic properties of the metals. It was determined therefore to make a series of experiments, keeping the primary current through the metal as nearly as practicable always of the same strength, but varying within wide limits the intensity of the magnetic field. We should in this way ascertain whether the transverse effect was simply proportional to the strength of the magnetic field, or was related to it in some more complicated manner.

By the term "strength of the magnetic field," as just used, is meant the intensity of the field between the poles which obtains when the metal plate is not in the field. This intensity is measured, as described in the article already alluded to, by withdrawing suddenly from the field a small coil of wire and observing the effect upon a galvanometer in circuit with the coil. This gives what is called the magnetic induction in this part of the field. In general, the magnetic induction in any magnetized space would be changed by introducing into that space a body capable of being magnetized by induction. The well-known expression for the magnetic induction within any such body placed in a magnetic field is (Maxwell's 'Treatise,' vol. ii. art. 428)

$$\mathfrak{B}=\mathfrak{H}+4\pi\mathfrak{J}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\mathfrak{H}$ is the *magnetic force* within the body (Thomson's 'Polar Definition,' reprint, p. 397), and $\mathfrak{J}$ is the *intensity of magnetization* (Maxwell, art. 384).

Now, in case of uniform magnetization, $\mathfrak{H}$ is equal to the intensity of the field as it would exist if the body magnetized by induction were removed (*i. e.* just what we measure by means of the coil and galvanometer), together with the force exerted by what we may call the magnetism induced on the surface of the magnetized body. This latter force will, of course, depend upon the shape and dimensions of the body. If it is a very thin disk, the reaction of the induced magnetism will, as Maxwell remarks, be equal to $-4\pi\mathfrak{J}$; and in this case, writing $\mathfrak{F}$* for the intensity of the magnetic field as above defined, we have

$$\mathfrak{H}=\mathfrak{F}-4\pi\mathfrak{J}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Substituting in (1), we have

$$\mathfrak{B}=\mathfrak{F}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

* Called M in previous article.

which means that, in a very thin disk magnetized by induction, the magnetic induction is just what it would be in the space occupied by the disk if the disk were removed from the field. Now the strip of nickel which we employ has a width 600 or 800 times its thickness; and it has been assumed that we may, for our present purpose, regard it as such an infinitely thin disk as Maxwell supposes. The error resulting from this assumption may easily be seen to be small. At the centre of the strip of nickel the real value of $\mathfrak{B}$ would be perhaps $\frac{1}{10}$ of one per cent. greater than the value as above determined. At a point 1 millim. from the edge of the strip the error might amount to $\frac{1}{3}$ or $\frac{1}{4}$ of one per cent.; while at $\frac{1}{10}$ millim. from the edge it would perhaps be two or three per cent. The average of the real values of $\mathfrak{B}$, therefore, at points along the line running across the strip from one side connexion to the other, is probably a rather small fraction of one per cent. greater than the value obtained on the assumption that $\mathfrak{B}$ is equal to $\mathfrak{H}$. This error is, to be sure, not constant; but it is nearly so up to $\mathfrak{B}$ = about 5000; and when it begins to change rapidly, it grows smaller.

Its influence upon the curve given further on must be very small. We assume therefore, as stated above, that by determining the strength of the magnetic field by means of the coil and galvanometer before the nickel is placed in the field, we ascertain with sufficient accuracy the value of the magnetic induction in the nickel strip itself when placed in the magnetic field. The advantage of determining this quantity is of course very great; for though we are probably unable to say what is the exact physical nature of magnetic induction, we do attach to the quantity represented by that term a very definite and important mathematical significance.

It was designed, therefore, to investigate the law of the variation of the transverse effect with the variation of the magnetic induction. Nickel was the best metal to experiment upon, for the following reasons: the strip of this metal at hand was very thin; the transverse effect appears to be essentially more powerful in nickel than in iron or cobalt; the magnetic permeability of nickel changes more rapidly than that of iron or cobalt with high magnetizing-powers.

As it was desired to determine simply what function of the

magnetization the transverse effect would prove to be, the primary current through the nickel strip has been kept approximately constant, the greatest variation from the mean being probably not many per cent., as will be shown further on. Within these limits it has been assumed that the transverse effect may be considered a linear function of the direct current.

It should be here stated that this latter relation has not yet been proved to hold rigidly even in a non-magnetic conductor like gold; and the matter must some time be investigated, though there seems to be no reason to think that the assumption, as above limited, can prove to have involved any considerable error.

The intensity of the magnetic field, and so the magnetic induction in the nickel plate, has been varied from about 1600 to about 10,000 in absolute (cm.-grm.-sec.) measure.

In the course of this investigation I have become indebted to nearly every one connected with the Physical Laboratory of the Johns Hopkins University, but particularly to Mr. S. H. Freeman, Fellow in Physics, and Mr. H. R. Goodnow, Special Student in Physics, who for a while carried on the experiments together. Mr. Freeman especially worked with me for a long time; and several suggestions of his in regard to the arrangement of apparatus and the method of experimenting were adopted with great advantage to the work.

In my last article on this subject the results of measurements were given in the form $\frac{M \times V}{E'}$, where M was the strength of the magnetic field*, V was the direct current divided by the section of the conductor, and E′ was the transverse electromotive force per centimetre of the width of the strip. In that article were given certain reasons for thinking the above quantity more likely to be a constant for any given metal than the quantity $\frac{M \times E}{E'}$, where E is the electromotive force per centimetre of the *length* of the metal strip. Recent developments, to be spoken of further on, raise the question whether the ratio $\frac{M \times E}{E'}$ will not after all prove to be the more fundamental and invariable quantity; but as E is rather dif-

* Called $\mathfrak{F}$ in this article.

ficult to determine with accuracy, and as in any given strip of metal V is likely to remain under ordinary conditions of temperature &c. very nearly proportional to E, the use of the former quantity will be retained for this article at least. The values of M [$\mathfrak{M}$] will be given separately, however; and, for convenience in plotting the results, the quantity $\frac{E'}{V}$ will be used instead of $\frac{V}{E'}$. The values of $\mathfrak{M}$ will, in plotting, be laid off as abscissas, and the values of $\frac{E'}{V}$ be taken as ordinates. This method of plotting gives a simple curve in the present case, and puts the results of the experiments in form to be compared with those of previous investigations of some of the magnetic properties of nickel. It is this quantity $\frac{E'}{V}$ which, after Maxwell, in accordance with the suggestion of Mr. Hopkinson*, is now called the "rotational coefficient" of nickel. Mr. Hopkinson has suggested "rotational coefficient of resistance;" and possibly some quantity might be found which would demand that title. At first sight $\frac{E'}{V}$, which is an electromotive force divided by a quantity proportional to a current, would seem to be of the nature of a resistance; but it is to be noticed that the electromotive force E′ is not the cause, but the effect, of the current implied in V.

In the experiments which I have described in previous papers, no account was taken of the temperature of the conductor experimented upon. When these experiments upon nickel, however, had been going on for a long time, it began to be suspected that the temperature of the room, and so of the nickel plate, did exercise a very considerable influence upon the magnitude of the transverse effect as expressed by the ratio $\frac{E'}{V}$.

* Phil. Mag. Dec. 1880, p. 430. Prof. Rowland has (Phil. Mag. April 1881, p. 254) remarked upon Mr. Hopkinson's note. Maxwell did not know any such effect to exist. In fact he expressly stated that it probably did not exist; yet, seeing the possibility of it, he let fall the phrase which seems now best fitted to define this newly discovered property of the metals.

A few hasty experiments with considerable ranges of temperature in the room indicated very decidedly that the temperature was a factor to be considered, and that the higher the temperature the greater the value of E′, other things being equal. The magnitude of this influence can hardly be determined from results thus far reached. It may prove that the transverse electromotive force E′ is no more increased by a rise of temperature than the direct electromotive force E* is; and in this case it would appear, as intimated above, that the ratio $\frac{E'}{E}$ is the one to be investigated rather than $\frac{E'}{V}$.

Future investigation must determine this matter; and meanwhile it has been sought to avoid evil consequences by regulating, as well as practicable, the temperature of the nickel plate. Sometimes an experiment had to be made at a rather high temperature for instance; and an attempt would then be made to balance this by making another with about the same strength of magnetic field but at a low temperature, or *vice versâ*. There was, however, even now no attempt to determine the actual temperature of the nickel; but a thermometer was hung up with its bulb close to the plate, and as nearly as practicable always in the same position with respect to the latter, and both plate and thermometer were protected from sudden changes of temperature. As the nickel was of course heated by the current, its temperature must have been always considerably higher than that indicated by the thermometer. Moreover this difference must have varied somewhat with the strength of the direct current; so that the temperature read can be assumed to give only a very rough indication of the *changes* in temperature of the nickel.

None of the numerical results of measurements made with nickel before the disturbing influence of temperature was discovered are here published. In some of the results afterwards obtained, however, the effects of variations of temperature can apparently be detected, as will be pointed out hereafter.

The general method of experiment has been already sufficiently described in previous papers. There will now be given

* Apparently E′ is in nickel affected by temperature more than E in most metals would be; but the rate of increase of the resistance of nickel with rise of temperature seems not to be known.

in tabular form the most important data involved in this examination of nickel, and the values of $\frac{E'}{V}$ obtained. The absolute strength of the primary current through the nickel strip in any case is not given, as, by the method of experiment, both the constant of the galvanometer used to measure this current and the horizontal intensity of the earth's magnetism at this galvanometer (this intensity being assumed to be constant during any one determination of $\frac{E'}{V}$) are eliminated from the formula for $\frac{E'}{V}$. There will be given, however, the tangents of the angles of deflection of the galvanometer-needle, in order to show about what were the limits of variation of the primary current. It may be well to state that this current was what one Bunsen cell would send through—say, six or eight ohms. It will be seen that there are variations of about 6 per cent. in $\tan \alpha$; and the actual variations in the primary current may possibly have been considerably greater than this; for on March 11th, 12th, and 14th the galvanometer stood in a different room from that in which it was placed for the previous observations, and the horizontal intensity of the earth's magnetism was probably somewhat different in the two places. I have, however, as stated above, assumed that within the limits of these variations the value of E′ is a linear function of the direct current. It is evident that no large error can result from this assumption.

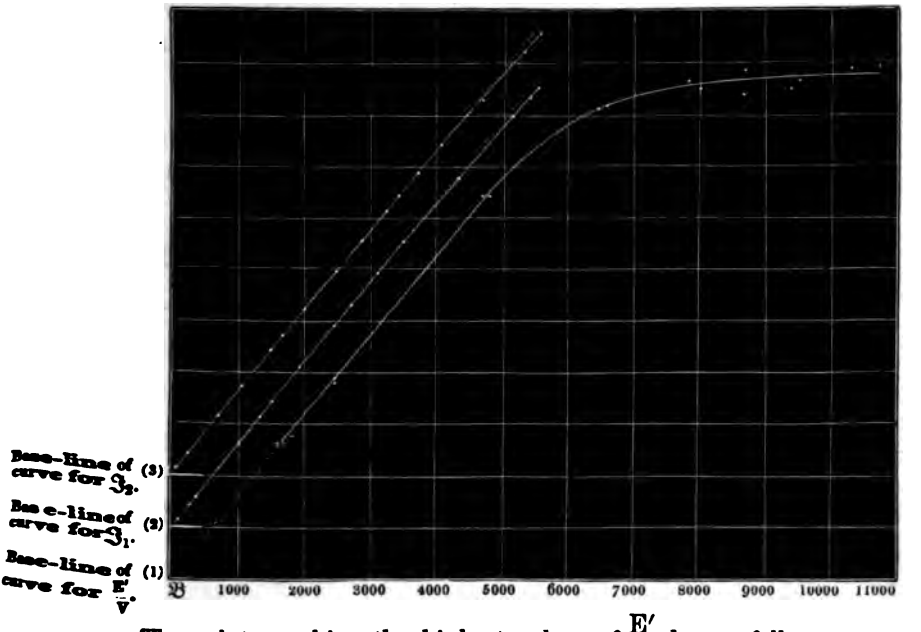
It will be seen from the table that the experiments began with the smallest values of the magnetizing force and went on by stages to the highest. This is the proper course to follow in order to avoid at any stage of the magnetizing force the effects of a previous stronger magnetizing force. It must, however, be stated that, before the series of experiments whose results are here published was begun, the nickel had already been several times subjected to a magnetizing force of about 7500, *i. e.* four or five times as great as the forces with which this series begins. The question, of course, arises whether there may not have been induced by this means a permanent magnetism sufficient to affect the results of subsequent experiments. In order to settle this question as far as possible, a small piece of nickel film, of the same quality as the strip in

use, was first subjected to the action of a field of about 7000 or 8000. It was then placed in a field of perhaps 1500 or 1600, whose direction was such as to tend to reverse any permanent magnetization which might have been induced in the film by the previous field. It was found that now in the second field the nickel became magnetized, temporarily at least, in the direction of that field. No attempt, I believe, was made in any case to detect the permanent magnetization. In this trial the small piece of nickel film was magnetized, not in the direction of its thickness, but in a lateral or longitudinal direction; so that we do not here have an exact parallel to the case of the strip; but it seems probable that magnetization in the direction of the shortest dimension would be much more easily disturbed than that in a longitudinal direction. Moreover, just before the series of experiments was begun whose results are here published, quite a long series was made with magnetizing forces about equal to those with which the published series begins; and this treatment would have tended, no doubt, to obliterate any traces of permanent magnetism due to the action of previous higher forces, even if this permanent magnetism had been much greater than we have any reason to suppose it was. On the whole, therefore, the probability of any considerable error from this source seems to be very small.

Date.	Temperature.	Tan α.	$\mathfrak{F}$ or $\mathfrak{B}$.	$\frac{E'}{V} \times 10^{10}$.
	°			
Feb. 24, 1881.....	18·5	·330	1667	209·3
25, „	22·0	·332	1655	211·1
26, „	21·5	·335	1664	208·1
26, „	16·0	·336	1735	213·2
28, „	19·5	·333	2512	314·3
28, „	20·0	·333	2512	307·0
Mar. 1, „	20·0	·330	4734	596·1
2, „	19·5	·327	4775	596·4
5, „	19·0	·338	6540	735·5
7, „	20·0	·339	6415	726·7
7, „	20·5	·340	7996	761·0
10, „	21·5	·324	7791	771·0
11, „	21·0	·342	8712	783·5
11, „	18·5	·343	8644	755·1
12, „	20·0	·338	9561	772·4
12, „	18·0	·338	9708	759·8
14, „	21·0	·326	10720	793·3
14, „	21·0	·323	10290	785·6

Galv. in new position.

Laying off the values of $\mathfrak{B}$ on the base-line, and taking the values of $\frac{E'}{V}$, plotted on a convenient scale, as ordinates, we have curve (1). It will be seen that this curve is nearly straight for a considerable distance, and that if this portion were extended backward it would pass very near the origin. Between the points corresponding to $\mathfrak{B}=5000$ and $\mathfrak{B}=8000$ the line tends strongly to the right, and thenceforward it continues as if asymptotic to some horizontal line not very far above.



The points marking the highest values of $\frac{E'}{V}$ do not fall so well in line as one might wish; but by looking at the table it will be seen that there were considerable variations of temperature accompanying these observations; and to these variations the irregularities can perhaps be in some part attributed.

We see now at once from the diagram that $\frac{E'}{V}$ is not proportional to $\mathfrak{B}$, the magnetic induction in the nickel. Can we find any magnetic quantity to which it is more simply related?

If we turn to the observations of Prof. Rowland on nickel*,

* Phil. Mag. Aug. 1873 and Nov. 1874.

we find that they can, as he says, be plotted in several ways. In order to compare them with the observations above given, we need to plot them in some manner that will lay off the values of $\mathfrak{B}$ (M in Prof. Rowland's first paper) on the base-line. We may then take as ordinates the values of the magnetic permeability, as Rowland has done in his first paper (plate iii.), or the values of κ, Neumann's coefficient of induced magnetization, or the values of $\mathfrak{H}$, the "magnetic force"* within the nickel, which would be a reversal of one method used by Rowland in his first paper (plate ii.); or, finally, we may use the values of $\mathfrak{I}$, "the intensity of magnetization according to the German theory," as Rowland calls it in his second article.

Having plotted these various curves we may compare them with (1) above, in order to determine whether our quantity $\frac{E'}{V}$ corresponds most nearly to μ, to κ, to $\mathfrak{H}$, or to $\mathfrak{I}$.

The curve for $\mu\left[\frac{\mathfrak{B}}{\mathfrak{H}}\right]$ will, long before $\mathfrak{B}$ has reached the higher values used in the curve for $\frac{E'}{V}$, have reached a maximum and returned nearly to the base-line. The curve for $\kappa\left[\frac{\mathfrak{I}}{\mathfrak{H}}\right]$ will be very similar to that for μ. We do not, then, find suggested a close connexion between μ or κ and the quantity we are studying.

The curve for $\mathfrak{H}$ bends *upward*, and is therefore quite dissimilar to that for $\frac{E'}{V}$.

The values of $\mathfrak{I}\left[\mathfrak{B}\frac{\kappa}{\mu}\right]$ obtained from two of Rowland's series†, made either with different specimens of nickel or with one specimen under quite varied conditions, give the curves (2) and (3). A separate base-line is taken for each of the three curves; and the ordinates of (2) and (3) have been plotted on different scales, in order to make the general inclination of those curves agree with that of (1). The values of $\mathfrak{B}$, however (and this is the essential particular in the plotting), are given on the same scale for all three curves. The important facts about

* Thomson's 'Polar Definition,' reprint, p. 397; and Maxwell's Treatise, art. 398.

† Phil. Mag. Aug. 1873, p. 153, and Nov. 1874, p. 327.

the lines (2) and (3) are that they are sensibly straight for a long distance, that they appear to come nearly straight from the origin, and that they begin to bend perceptibly toward the horizontal when $\mathfrak{B}$ becomes 4000 or 5000. Although these lines are carried only a short distance beyond this region, we can yet be sure that the bend is not due to faulty observations; for to make an error of 1 per cent. in the value of $\mathfrak{I}$ at this point would require an error of very many per cent., say 20 or 30, in the value of μ as determined by Prof. Rowland. From the manner and rate at which μ was changing at the points where his experiments ceased, it seems almost certain that these lines would continue to bend, and for a time to bend rapidly. Indeed the curve in which Prof. Rowland has continued μ beyond the range of his experiments would indicate that the curves (2) and (3), if continued a short distance further, would turn downward and approach the base-line. This, however, would mean that the magnetization $\mathfrak{I}$ actually *decreases* after a certain point with *increase* of the magnetizing-force. The possibility of this is spoken of by Rowland*; but there seems to be no experimental evidence of such an effect; and if it does not exist, it appears altogether probable that the lines (2) and (3) would become asymptotic to horizontal lines lying considerably higher than any points reached by the curves as here given.

We can therefore say that, so far as actual experiments have gone, there seems to be much tending to prove a very simple and intimate relation in nickel between the transverse effect and the "magnetization according to the German theory."

It would, of course, be desirable to test for some more minute agreement than has yet been traced between the curves for $\frac{E'}{V}$ and $\mathfrak{I}$; but such a testing would probably be difficult to make. An exact agreement could not be expected; for it would probably be almost impossible to obtain exactly the same quality and condition of metal in the very different shapes required for experiments on $\mathfrak{I}$ and experiments on $\frac{E'}{V}$.

There are, however, certain minute characteristics which would belong to all curves for $\mathfrak{I}$. Thus (2) and (3) should not

* Phil. Mag. Nov. 1874, p. 322.

be straight at any point. They are lines of double curvature, the steepest part of each being not far from $\mathfrak{B}=2000$. The curvature in this region, however, is very slight; and to detect a corresponding curvature in the line for $\frac{E'}{V}$, if such exists, would be a matter of considerable difficulty, though not, perhaps, impossible.

Having gone thus far with nickel, we might, were it not for the anomaly presented by the sign of the rotational coefficient in iron and cobalt, make a prediction by analogy as to what would prove to be the character of the curves for $\frac{E'}{V}$ in these metals. We should say that they would be sensibly straight for a much longer distance than the curve for nickel, and that in fact it might be difficult to carry the magnetization far enough to detect any marked departure from a straight course. So great a difference in behaviour as is indicated by a reversal of the sense of the transverse effect, however, makes any such predictions hazardous.

This difference of sign in the rotational coefficients of the magnetic metals is so anomalous and so important a fact, that one returns again and again to its consideration. Quite recently the determination of this sign for all three metals has been made anew. I have now tested, in all, four plates of iron (three of them having been cut from the same sheet, but the fourth being of a different thickness and probably of a somewhat different character), two plates of nickel (certainly very different from each other in condition), and one specimen of cobalt. With all these the record is perfectly consistent. Nevertheless it would be desirable to examine more specimens, and those differing widely in character. Different experimenters have observed many peculiar effects in iron under the influence of magnetism and the electric current, magnetism and mechanical strain, or the combined influence, which in a certain form we have here, of all three; and these effects appear to differ greatly, and sometimes to be of different signs, in soft iron and hard iron or steel. Thomson has found* that, under conditions of the above character, soft iron and nickel are, in certain apparently very important particulars,

* Phil. Trans. May 1878.

opposed in behaviour. I have looked in vain through all the facts of this kind with which I am acquainted for any plausible explanation of the fundamental phenomenon of the transverse action, nor can it be said that any clue has been found to the cause of the diversity observed. Nevertheless the opposition which Thomson has found in the behaviour of soft iron and nickel, under conditions of magnetism and mechanical strain, furnishes an analogy which should not be lost sight of. Thomson has moreover noticed that the effect which he was studying in soft iron became reversed in this metal at a very moderate value of the magnetizing force. It might be well to test the direction of the transverse effect also with very small intensities of the magnetic field.

An extended examination of the effect in iron and cobalt, similar to that which has been made in the case of nickel, should be undertaken as soon as practicable. It will require very great intensities of the magnetic field and a very large battery* to carry these metals through a range of magnetiza-

* In the experiments here detailed, the largest battery used has consisted of 48 large Bunsen cells arranged 8 in series. The resistance of each cell was probably something more than an ohm; the resistance of the electromagnet is, I think, rather less than an ohm. The resistance of the connexions was considerable, however; and the battery probably gave about its best effect.

After this powerful battery had been applied to the electromagnet, a rather singular effect was observed on returning to the use of weak currents. In making observations in the usual way to determine the strength of the field produced by these weak currents, it was found that the impulses given to the galvanometer-needle were very capricious. These observations may be arranged under two heads, + and −, according to the direction of the current through the electromagnet, this current being usually reversed after each withdrawal of the little coil from between the poles. The observations being arranged in this way, it would be found that there were occasional sudden changes of many per cent. in the readings in the same column. Of course the most obvious explanation of the phenomenon was that some connexion was loose, either in the circuit of the galvanometer and the test-coil or in that of the electromagnet. That the fault was not in the former circuit was made probable by the fact that by means of the earth-inductor, which was in the same circuit, quite uniform deflections of the galvanometer-needle were produced. To test for a fault in the magnet circuit, a tangent-galvanometer was introduced into it and its deflections observed during the series of observations on the strength of the field.

The readings of the tangent-galvanometer decreased slowly with the

tion corresponding to that through which nickel has been examined. It seems doubtful whether the magneto-electric machine can be here employed, as the current which it produces may not be sufficiently uniform to be used with advantage.

The examination of the non-magnetic metals also should be continued as fast as circumstances will permit, with the object of determining the sign and, when practicable, approximately the magnitude of the rotational coefficient in every case.

In my article of last November I stated that, in accordance with Prof. Rowland's suggestion, I had tested the Kerr effect with one specimen of nickel, and found it to be of the same sign as the effect which Kerr had observed with iron. In order to prevent mistakes, the experiment was repeated with iron, or rather, I suppose, with steel, the result being the same which Kerr had obtained. The surface of nickel first used in this way was the coating upon one of the plates of Prof. Rowland's absolute electrometer, the metal beneath being brass. Two other specimens of nickel have since been tried. One was a coating deposited electrolytically directly upon the iron pole of the electromagnet, the other was a nickel film fastened with soft cement to a plate of glass. Probably none of these specimens was pure; but (and this is a matter of more importance) the third was of precisely the same character and origin as the specimen in which the transverse effect was studied. The Kerr effect is of the same sign in all three plates of nickel, *i. e.* of the same sign as the effect in iron.

One specimen of cobalt has also been tested for this effect.

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running-down of the current; but the changes were quite regular, and not at all of a character to account for the irregularity of the other observations. The most plausible explanation I could finally propose was, that this irregularity in the strength of the magnetic field was due to a sort of uncertain struggle between the action of the present weak magnetizing current, and the magnetization previously induced by the strong currents in the poles of the electromagnet, which are not, I believe, of very soft iron, and are probably capable of considerable permanent magnetization. I do not by any means feel able to assert, from my rather hasty observations, that there can be no other explanation. I have, however, simply thought the matter of sufficient importance to justify me in recording what seemed to be the fact.

A block of cast cobalt, quite similar to that from which was cut the cross mentioned in the first part of this article, was sawn in two, and one of the fresh surfaces was made quite smooth with a file and then polished with emery. It is not difficult to get a sufficiently good surface. An hour's work might prepare it.

With sunlight and a tolerably strong magnetic field, say 4000 (cm.-grm.-sec.), the rotation produced by cobalt was detected, and found to be of the same sign as that observed with nickel and iron.

The fact that nickel behaves like the other magnetic metals in optical effect, but differently from them in the transverse electrical effect, is on its face undoubtedly an argument against the theory which refers the two effects to the same cause. In order if possible to examine the optical effect in a somewhat different manner, an attempt has been made to detect an action of magnetized nickel upon polarized light transmitted directly through it. For this purpose a thin piece of glass was coated over a part of its surface with nickel by Wright's process*, the action being stopped before the nickel film became thick enough to be opaque. It was found, however, that the glass alone, although only about $\frac{1}{6}$ millim. thick, perceptibly rotated the plane of polarization of the light sent through it when subjected to the very strong magnetic field employed. The action produced by the nickel and glass together was of the same sign as that produced by the glass alone; and as the magnitude of the effect could not in either case be measured with any accuracy, the experiment was quite negative in result. I now, however, took a glass tube, fused the end, and blew out the bubble till it burst. A piece of the exceedingly thin film thus obtained was subjected to the action of the magnet, and most strenuous endeavours were made to detect its action upon the beam of polarized light. This action must have been exceedingly slight, though there is some evidence, which it is not necessary to give, that it was detected. The glass, however, was coated as the first piece had been, and again with its coating subjected to the action of the magnet. The trial was, for certain reasons, rather unsatisfactory; and although no rotation of the plane of polarization was now detected, I do

* Amer. Journ. of Science, Jan. 1877, p. 49, and Sept. 1877, p. 169.

not think this fact can be taken as evidence that the effect of the nickel had counterbalanced the effect of the glass. Both these experiments on direct transmission have been, we may say, quite negative; but these details are given as marking out a line of research which will probably be some time resumed.

An endeavour has also been made to detect a possible rotational effect due to reflection from silver when strongly magnetized*. For this purpose two strips of silver upon glass were used; and these strips were fastened one upon each pole of the magnet, the silvered surfaces being turned toward each other and as nearly parallel as practicable. The poles being brought near together and the light being let in between the silvered surfaces at a large incidence, it was possible to obtain twenty or thirty successive reflections before the beam emerged toward the analyzing Nicol. Certain difficulties were introduced by this arrangement; but in spite of these I think that, if the action of silver had been one tenth as strong as that of iron, the effect would have been detected. No such effect was observed.

XXXIV. *On the Results obtained from a Modification of Bunsen's Calorimeter.* *By* Prof. B. STEWART *and* W. STROUD†.

A DESCRIPTION of this instrument was brought before this Society on June 26, 1880, and afterwards appeared in the Proceedings of the Physical Society, vol. iv. p. 52, and Philosophical Magazine, vol. x. p. 171. The results obtained at that time were not very good, owing greatly to the large bore of the capillary tube, which necessitated the use of a large quantity of substance, the consequence being that the mercury in the bulb was so much heated that the loss of heat by radiation was not inappreciable during the time of performing the experiment.

Since then a new instrument has been obtained from Mr. Casella, having a much finer capillary stem with an empirical scale engraved on it. By means of it very good results have

* In this experiment I had the very efficient assistance of Mr. Arthur W. Wheeler, Fellow in Physics, whose untimely death is so deeply lamented.

† Read June 26, 1881.

been obtained with very small quantities of substances; in fact, it has been found (within certain limits) that the smaller the mass of the substance the better.

At first we endeavoured to make allowance for the loss of heat during the experiment by constructing a curve of cooling, and adding to the rise obtained by dropping in the substance the amount that had been lost while the experiment was being performed, according to the curve of cooling. This method, however, did not yield good results.

Our final method of operating is comparative only; that is to say, one metal, whose specific heat is accurately known, is chosen as the standard to which all other substances are referred, and, in order that the conditions may be the same in all cases, we first ascertain the rise obtained by introducing a given weight of mercury at a given temperature (that of the air), and when the instrument has cooled throw in the substance whose specific heat is desired. During the two experiments the temperature of the air is usually nearly constant; and in that case no correction for temperature is required.

A second point to be noted, is to put in such a weight of substance as will produce about the same rise as was obtained with the mercury. It is thus possible to make the determination of the relative specific heats under almost precisely the same circumstances, a condition which is eminently conducive to good results.

In practical working with the instrument the following hints may prove useful :—

1. The test-tube is always filled with water to the same height before being cooled, this height being that of the level of the copper or slightly above it.

2. About ·6 grm. of mercury is placed at the bottom of the tube, unless the substance to be experimented on is attacked by mercury. The object of this is to allow the solids that are introduced to part with their heat more freely. The substance comes thus into much more intimate heat-contact with the mercury of the thermometer than it would if it rested upon the glass alone. If, for instance, some pieces of sulphur are allowed to fall to the bottom of the tube, they sink partly into the mercury, and quickly give up their heat to it, so

that it is more nearly the same as if the mercury had been heated.

3. A large-sized box is employed, in which plenty of ice is placed, so as to completely surround the instrument.

4. As the mercury sometimes moves very sluggishly, gentle tapping, not vertically, but horizontally, has been found very beneficial.

We will now take an example to illustrate the method of working :—0·396 grm. of mercury was weighed out and allowed to remain for some time in contact with the bulb of a thermometer. Meantime the instrument was gently tapped and the height read. The mercury was then poured in after the thermometer-reading (18°·6 C.) had been taken. The rise obtained on the scale was 15. An experiment with iron was then made ; and since the specific heat of iron is about four times as great as that of mercury, ·144 grm., or about one fourth the weight of the mercury, was taken. The temperature was still 18°·6 ; and the maximum rise obtained was 18 ;

$$\therefore \text{ specific heat of iron } = \cdot 0333 \times \frac{18}{15} \times \frac{396}{144} = \cdot 110.$$

The following results have been obtained :—

Substance.	Weight.	Temperature.	Rise.	Specific heat. Hg=·0333.
Mercury	·364	16·8	15	
Sulphur	·148	17·1	32	·174
Mercury	·325	16·2	10	
Iron	·144	16·3	15	·110
Sulphur	·134	16·2	22	·178
Mercury	·396	18·6	15	
Iron	·144	18·6	18	·110
Sulphur	·081	18.6	16	·174
Mercury	·400	18·0	14·5	
Iron	·144	18·0	18·0	·115
Sulphur	·083	18·0	15·5	·175
Mercury	·505	15·8	14·5	
Iron	·145	16·2	13·5	·112
Sulphur	·118	16·2	17·0	·177

		True.
Mean specific heat, iron.....	·1118	·1138
„ sulphur	·1756	·1776

PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

NOVEMBER 1881.

XXXV. *Note on the Index of Refraction of Ebonite.* *By* W. E. AYRTON *and* JOHN PERRY*.

IN a note communicated to the Royal Society (printed in 'Nature,' No. 596, vol. xxiii. March 31, 1881), we described how, by using a selenium cell, lent us by Mr. Bidwell, and a pair of delicate Bell's telephones, we had succeeded in showing, 1st, that there was refraction when intermittent radiation from the oxyhydrogen light passed through an ebonite prism; and, 2ndly, that the index of refraction of that ebonite was approximately 1·7.

Exceedingly great care had to be taken, in consequence of the feebleness of the sounds given out by the telephones; and, from the nature of the experiment, we obtained the index of refraction for that narrow band of rays which experienced least absorption.

Shortly after these results were published, Prof. Fitzgerald, of Dublin, suggested, in conversation, the possibility of checking them by measuring the polarizing angle of light reflected from ebonite, on the assumption that the refracted ray is at right angles to the reflected one when giving maximum polarization. Subsequently Dr. Jellett was so kind as to make these experiments, the results of which Prof. Fitzgerald per-

* Read June 25, 1881.

mits us to quote. The mean index of refraction for ebonite thus obtained, on Fresnel's theory, was 1·611.

Later on we repeated our selenium experiments, replacing the intermittent oxyhydrogen light with an intermittent electric light, and increasing the electromotive force in the selenium telephone-circuit to about 60 volts. A confirmation of our former result was obtained; but, although we were able to take greater precautions to ensure accuracy, we obtained no more than a confirmation; and from the difficulty of hearing the weak sounds in the telephones, we felt that the index of refraction thus measured might be as much as 1·8 or as small as 1·6.

In the course of these experiments, however, it was noticed that visible red rays were certainly refracted; and consequently we proceeded to make measurements according to ordinary optical methods, using the apparatus shown in the figure. L (fig. 1) is a fairly powerful electric light produced by a Gramme machine; C is a glass lens giving a parallel beam of light, part of which passes through the slit, S, $\frac{1}{20}$ inch wide, and falls on the edge of the ebonite prism P. F is a frame

Fig. 1.

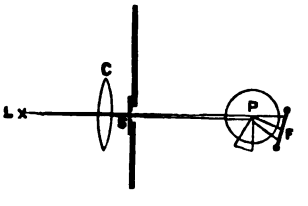
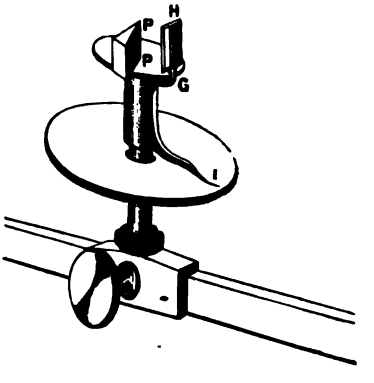


Fig. 2.



holding tissue-paper, which can be moved about P as centre, and which carries an index, I, pointing to the graduations on the circle, as seen in fig. 2. There was a fine vertical line in the middle of the tissue-paper; and HG, forming about one third of the paper, was well blackened. First this screen was moved into such a position that the edge of the prism threw a

black shadow which was bounded by the fine central line, and between that line and the blackened portion H G was a thin band of white light. In fact a narrow beam from the slit fell on the edge of the prism; and half was stopped by the prism, the other half going on. The index-reading in this position was taken; and now the screen was moved round until a red spectrum was seen. At the least-refrangible end this spectrum terminated nearly abruptly, as the ordinary visible spectrum usually does; and this end was made to coincide with the central line in the screen, and the index-reading taken when, after moving the prism itself, it was supposed that we had minimum deviation. The index-reading was also taken in the same way for the most-refrangible end of the visible spectrum; but as this did not die away at all abruptly, and as the whole spectrum was very faint, the second set of measurements merely gives a rough idea of the amount of spectrum that was visible. The mean of a number of observations made by different observers, and the results of which were closely in accord, gave 1·66 as the index of refraction for the well-defined least-refrangible end, and 1·9 as the average result for the badly-defined most-refrangible end.

As the slit in the metal diaphragm used with the selenium experiments had to be much wider than that employed with the simple light-experiments, we cannot of course tell what exact part of the spectrum produced the sound: probably it was at about the least-refrangible end of the visible spectrum; but it may have been the dark rays just beyond.

Summing up the results of the various experiments, we have for the index of refraction of certain specimens of ebonite:—

Ebonite prism, selenium, and telephones . .	about 1·7
Measurement of polarizing angle by reflection	„ 1·611
Least refracted end of visible spectrum produced by ebonite lens having an angle of 28°·5 .	about 1·66

In a paper by Captain Abney and Colonel Festing, recently read before the Physical Society and printed in the Philosophical Magazine for June, on the Transmission of Radiation through Ebonite, reference is made to our original experiments; and the authors say that, judging from the figure accompanying our Note, they should think that the thickness

of the ebonite prism traversed by the intermittent beam must have been about one fourth of an inch. We are afraid that that figure is liable to give this misconception; in drawing it we were merely paying attention to the directions of the incident and refracted beam, and not to the actual thickness of the ebonite, which was in fact very small indeed where the intermittent beam passed through it.

XXXVI. *The Microphonic Action of Selenium Cells.* *By* Dr. JAMES MOSER*.

WHEN I began these researches on the Transformation of the Energy of Light into that of Sound by the Photophone, I held the opinion which is still common, that there are two kinds of photophones and three forms of light-rays. My experiments led me to the conclusion that there is only one way in which light acts photophonically. The effect of radiation on selenium cells is, in fact, the same as that exerted on the majority of solid, liquid, and gaseous bodies used as non-electric photophonic receivers. Though rays may have different wave-lengths, all rays are the same in kind. There are not three kinds—heating, luminous, and chemical, but one and the same ray may have heating, chemical, and luminous effects.

In February last, when I began these experiments, I believed that the photophone could inform us as to the direct correlation between light and electricity. A current circulating around a beam of polarized light changes the plane of its vibration. Hence we are led to conjecture that there may exist further relations between light and electricity, and that, as the electric current or lines of magnetic force affect the beam, so, inversely, the beam may influence the electric current or the magnetic lines of force; and we may conjecture that such influence may manifest itself in the photophone.

I therefore tried to change the magnetic condition of an iron plate by light. I hoped, for instance, to get an electric current in the coil of the telephone at the moment when

* Read June 25, 1881.

its iron plate is exposed to radiation. I did not succeed in observing such a current.

Prof. W. G. Adams was the first to show that selenium on illumination develops an electromotive force. Still supposing that in the photophone a direct correlation between the energy of light and that of the electric current might reveal itself, I endeavoured to observe and to measure the electromotive force developed in selenium cells on their exposure to light.

I made selenium cells according to the method of Bell and Tainter as modified by Bidwell. Two thin copper wires were wrapped parallel side by side several times round a strip of mica. Selenium was then melted, and crystallized between them. In this way I obtained cells which were very sensitive and yielded, when connected with the battery, a clear sound in the telephone. According to my last measurement, the resistance of one of those cells in the dark is 3000 ohms, diffuse daylight reducing it to 2700. The measurements were made with an astatic-mirror galvanometer, the resistance of the coils of which was 6860 ohms. The scale was about one metre distant from the mirror, each division one fortieth of an inch. There were other galvanometers at my disposal, and a battery of twenty Leclanché cells. The galvanometer proved itself more sensitive than the telephone.

The above-mentioned selenium cell yielded by intermittent radiation of lime- or electric light clear and distinct sounds; illumination by the same sources of light deflected the image of the slit strongly.

But the same light which, when a current of an external battery flows through the cell, makes the telephone to sound or the spot of light to slide along the whole scale, is not able to produce an observable electromotive force in the selenium cell. This non-appearance of a current (the circuit being formed only of selenium cell and galvanometer, or of selenium cell and telephone) is, in my opinion, very noteworthy; for the problem which I wish here to solve is not to make photophones without batteries, but to explain the efficiency of the selenium cells by the qualities they actually possess.

It is possible to prepare pieces of selenium which show an electromotive force on being illuminated. I shall return to

this point further on. But cells and pieces of selenium *not* possessing this property nevertheless show photophonic action. Therefore the photophonic action cannot be explained by this property, which is, or at least may be, wanting in the selenium cells.

I proceeded further, always endeavouring to find a correlation of the energies. The current flowing through a selenium cell experiences a counter force—a polarization. I tried to observe, and, as far as possible, to measure it. This polarization is shown by *all* my cells and preparations of selenium. I found it, however, when measured by the compensation method, to be only about the thousandth of a volt. In order to observe the polarization as near as possible to its maximum, I employed a rotating switch, which I constructed by means of two alternating tooth-wheels, and which changed the current eighty times per second.

I next endeavoured to increase the electromotive forces originating in the selenium cell, as well as those produced eventually by light. I tried to attain this by taking the two wires of different material; then I prepared selenium pieces where selenium was simply between two straight parallel wires. At first I made a selenium cell, just like the one described above, replacing, however, the one copper wire by one of platinum, so that the selenium was between copper and platinum. But the polarization, which again could be easily observed, was here also very small. On measuring, it was found again about one thousandth of a volt. Also this cell did not produce, either in the dark or on illumination, any current which could be observed by the galvanometer.

In order to increase the polarization, I gave the polarized selenium cell greater capacity. I took, instead of the wires, two larger plates, each 6 centim. long, 3 centim. wide, and about 1 millim. thick. My intention was to begin the experiments with three of such pairs, with

copper, selenium, copper;
zinc, selenium, zinc;
zinc, selenium, copper.

With the latter of these cells I succeeded (after having sent through it the current of a strong battery) in observing

a polarization of about 0·4 volt. The cell had now become a polarization battery, giving rise to a current long after it was separated from the primary battery.

In all these experiments, and especially in the last, a superposition of polarizations could be distinctly observed; so that here we have to deal, not simply with thermo-electric currents, but with electro-chemical decomposition.

An observation, however, which I now made gave a different direction to these researches. But their aim remained unchanged—namely, to explain the efficiency of the selenium cells, to understand the transformation of energy of light into that of sound in the selenium cell, regarding it from a more general point of view and not merely as an isolated phenomenon in selenium, but, by finding the general law, to remove selenium from its isolated position. This, however, may be done either by comparing other bodies with it (which is the method of previous investigations on the subject, and was my own also till now), or this may be effected by inserting selenium in the series of other bodies. The latter method I shall now describe.

I intended to make such cells of copper, selenium, copper, or of zinc, selenium, copper plates, in the same way as the above-described photophonic cells. On a copper plate I melted amorphous selenium, and put on it the second metal plate of zinc or copper. Then I heated gradually, so that the selenium became crystalline; and I then annealed it. Whilst the amorphous selenium adheres very well to the metal plates, these cells proved very brittle when the selenium was crystalline; the selenium always split off from the copper plate. In order to find how to avoid this splitting-off, I examined the matter more closely; thus, I left out the second metal plate, and experimented with copper and selenium only.

The preparation was, in accordance with that of the photophonic cells, the following:—One of the copper plates to be used for the cells was heated on a large brass plate of about 3 millim. thickness; this was covered by a thin sheet of mica, on which the selenium which eventually flowed off was collected. The copper plate having reached the melting-point of amorphous selenium, was covered with this substance and thereupon removed from the brass plate. On being re-

moved it cooled quickly; and on it now a black brilliant layer of amorphous selenium remained. The larger brass plate having also cooled, the copper plate covered with selenium was again laid on it and again slowly warmed, so that the selenium crystallized. The temperature was still further raised, near to the point at which the crystalline selenium begins to melt. The selenium was then annealed.

But, notwithstanding this caution, it was not possible to fix the selenium on the copper plate. It exfoliated and split off. Every lamina which exfoliated was on the upper side light grey, and on the lower side blue-black, not brilliant but dull. In the same way the copper plate had now a similar dull blue-black covering. This blue-black body is cuprous selenide, Cu_2Se. There were thus three layers—copper, cuprous selenide, and selenium; and in the copper-selenium-zinc cell two other layers—selenide of zinc and zinc; so that all together there were five layers.

I took thinner copper plates; but the splitting-off still occurred.

This experiment shows that between the copper and the selenium, or rather the cuprous selenide, there is only a slight and imperfect contact.

But the same is the case in the photophonic cell. In this also the three layers—copper, cuprous selenide, selenium—follow one after the other. The plates give only an enlarged view of what is to be observed in the photophonic cell on a smaller scale, and with more difficulty, by the eye. Thus we see that in the photophonic selenium cell also we have only a similar slight and imperfect contact, which is to be influenced by radiation. It was first by this experiment that it became obvious to me that a microphonic effect is the essential part of the action of the selenium cells.

I was confirmed in this conclusion, that *the selenium photophone is a microphone*, when I learned that Mr. Sumner Tainter had constructed a photophone in which selenium was replaced by carbon. Indeed his apparatus, the zigzag line filled with carbon on the silver-coated glass plate, is nothing else than a microphone. If we remember the apparatus described by Mr. Hughes as a thermoscope, we understand that the selenium photophone of Messrs. Graham Bell and Sumner Tainter

agrees in its principle with the carbon photophone of the latter; and, again, this is in its main features the same as the thermoscope.

Thus my attention became now more directed to those passages in the literature where the degree of the resistance at the surfaces of contact between the selenium and the metal, in comparison with the total resistance, is discussed.

In 1875, before the invention of the microphone, Dr. Werner Siemens observed a high resistance at the surfaces of contact. He arrived at the conclusion "that an essential part of the resistance of the selenium is in its limiting layers at the surfaces of contact"*.

Mr. Sabine is of the same view. Finding, *e. g.*, in one piece of selenium with several transversal platinum wires the resistances of the junctions to be 429, 479, 498, and 428 megohms, the resistance of the selenium itself between the wires, however, much smaller (22, 13, and 0 megohms), he remarks:—"It is clear from these measurements that a large portion of the observed resistance of a so-called selenium resistance may, and frequently does, reside in the junctions, and not in the selenium. Therefore the larger we make the surface of contact between the platinum and the selenium, the less likely are we to find an otherwise sensitive piece of selenium rendered comparatively insensitive by the introduction of high junction resistance. In this respect the form of selenium plate designed by Dr. Werner Siemens, in which the platinum wires form gratings or interlying spirals, is unquestionably the best form to employ when the object in view is to obtain a high sensitiveness to light"†.

Both authors assume the selenium to possess a special sensitiveness, and this quality to be damaged by the high resistance of the junctions. Therefore they aim at annihilating this resistance at the surfaces of contact. Aiming at this annihilation, they enlarge the surfaces of contact and thus diminish the resistance.

The surfaces of contact should indeed be enlarged. The reasons, however, for which this must be done are, in my opinion, just the opposite to those influencing these two

* Pogg. *Ann.* clix. p. 140.

† 1878, Phil. Mag. (5) v. p. 404.

observers. It is the high resistance at the junctions which is the variable, and which is necessary for the microphonic action. The case of this resistance alone being the variable I shall discuss immediately. That the resistance at the junctions is high is a necessary consequence of the imperfect and variable contact. To annihilate it is to render the photophone insensitive. And, *vice versâ*, the more extensive the surfaces of contact are, the more sensitive is the selenium cell.

A further strong support, amongst others, is given to this theory by the observation of Mr. Bidwell *, who has made very numerous experiments with selenium cells. "He got the best speech from cells of high total resistance . . . The selenium should, however, have a low specific resistance."

These observations are easily understood by the microphonic action of the cells; for, that the total resistance is to be great and yet the specific resistance of the selenium is to be small, has no other meaning than that there must be a bad contact between good conductors.

The next question is, if this microphonic action is confined only to the surfaces of contact. I must here recall that Messrs. Draper and Moss †, distinguishing three crystalline modifications of selenium, observe as to their conductivity, "Between these two forms of granular selenium—the apparently nonconducting and the comparatively highly conducting—there is another, of intermediate resistance. This modification is highly sensitive to light."

Just so, according to Rammelsberg ‡, selenium exists in four allotropic modifications, three of which are crystalline.

For evidence of the microphonic action I was at first contented to observe that selenium in this crystalline state, in which it is most brittle and the most powdery, is also most sensitive to light. Afterwards I succeeded in obtaining a piece which shows this very clearly. Between two platinum wires of 3 centim. length was a selenium plate 8 millim. in width and hardly 1 millim. in thickness. Heated in air and annealed, the whole surface had taken the light grey colour of a crystalline state; half the upper surface, on

* London Phys. Soc. Jan. 22, 1881; Tel. Journ. ix. p. 52.

† 1873, Proc. Irish Ac. (2) i. p. 533, Nov. 10.

‡ 1874, Pogg. *Ann.* clii. p. 151.

the side of the one platinum wire, was smooth and continuous; the other half, near the other platinum wire, was powdery and granular. Alternately one of the two halves was kept constantly dark, and the other half at the same time intermittingly illuminated. Thus I could observe that almost the total sensitiveness of the whole plate resided in the granular coarse half of the surface. This shows that microphonic effects occur also in the selenium itself. But even if the selenium were perfectly homogeneous, and remained so during the illumination, the rays would produce heat and change of volume, which would have a microphonic influence on the contact.

By such microphonic changes the efficiency of the selenium cell would be explained, and thereby the selenium would be removed from its isolated position and coordinated with all the other bodies in which change of volume and of form under the influence of radiation have been observed.

I, however, do not deny that light may have other effects on the selenium. That such is the case is indeed one of the causes which have hitherto masked the microphonic action of the cells. That my present view of the simple action of the selenium did not present itself at once is owing to two causes.

In the first place, there is the fact that the microphonic variations or changes in volume and in form, attributed commonly to the so-called heat-rays, are produced in the selenium by the illuminating rays.

In the second place, complication is introduced by the fact that selenium exists in four allotropic modifications, and that light is able to exert on these divers influences. Though these are not essential to the action of the photophone, it has nevertheless been assumed by others, and at first by myself, that such changes might be the key for the explanation of the selenium photophone.

Of these two impediments which stood in the way of the perception of the microphonic action of the cells, I intend to speak more in detail. And first a few words on what, for the sake of brevity, may be called the heating effect of the light-rays.

In the beginning of April* I repeated the experiment of Mr. Graham Bell, and allowed light to pass through ebonite.

* Lond. Phys. Soc. April 9, 1881; 'Nature,' xxiii. p. 595.

In order to be able to make a quantitative observation I connected the selenium cell, on which the light was to fall, not only with the telephone, but also with a galvanometer. While, however, it appeared that a photophonic effect took place through the ebonite, it was shown that this effect was only a small part of the direct effect when the ebonite diaphragm was away. Now, as ebonite allows passage only to red and ultra-red rays, we learn from this experiment two things:—

(1) That the illuminating rays are those which are especially absorbed by selenium, and that these produce the greater part of the photophonic action.

(2) That it is even possible to make *a selenium photophone without light*—that is, with exclusion of illuminating rays and by the influence of heat-rays only.

That there is simply a heating effect of the illuminating rays in the selenium photophone has perhaps not yet been sufficiently insisted on, because the most modern researches on light-rays are not yet assimilated to the general view of physics. We find still the conception of three different kinds of rays—heating, illuminating, and actinic; whilst it has long been demonstrated that there is only one form of rays, differing from one another, however, in wave-length and intensity. On the body on which the ray falls depends whether its energy is perceived as heat, or light, or chemical effect. In order to be effective a ray must be absorbed. The bodies, however, on which the rays fall select the rays they absorb in the most various manner, which we recognize by the endless varieties of absorption-spectra. The absorbed rays alone are able to exert an effect; they only can warm the body. And heating occurs not only by red and ultra-red rays, but by the rays which are absorbed. Only the absorbed rays can produce (and that is the point in question here) changes of volume and of shape, and in this way influence the contact of current-conducting parts.

As the last-mentioned experiment demonstrates, selenium absorbs principally the illuminating rays. When, therefore, selenium is exposed to radiation, the change of volume and of shape is produced chiefly by the illuminating rays; *selenium is heated by light.* It must be the illuminating rays which make the selenium cell act microphonically.

That light, however, may produce in selenium other changes than heat and deformation, which are essential to the efficiency of the selenium cell, has been the second cause which masked the microphonic action of the cell. These are changes in the material; they concern rather the chemistry of selenium. They are indeed purely chemical if we view the existence of selenium in four allotropic modifications as a chemical quality. Into these chemical changes I shall enter here only so far as it is necessary for the proof that they are not essential to the microphonic action of the selenium cells, since my aim now is the physical one of correlating two forces.

When, now, we no longer consider the selenium cells especially, but selenium in general, we find that light can produce in it, if the selenium is an element and pure*, no other chemical changes than those which induce the transformation of one of the allotropic modifications into another one. But such a transformation is connected with development of energy; for in 1851 M. Hittorf† observed a rise of temperature of 90 degrees when the vitreous modification changed into the crystalline; and Regnault‡ (1856) in a similar case, observed an elevation of temperature of 130 degrees. With a proper arrangement (that is, in a closed circuit) we shall get, instead of the development of heat, an electric current—just as, for instance, two solutions of the same salt, but of different concentration, on being mixed together, give a development of heat, but, when brought into a circuit in a proper manner, produce electricity equivalent to this heat.

I have already mentioned above that Prof. W. G. Adams thus observed electromotive forces on illuminating selenium connected only with a galvanometer, but that generally the photophonic cells do not give such a development of electricity, and that therefore this property of selenium cannot be used

* On melting selenium, a grey film was formed on the surface. This being removed by a platinum spatula, the amorphous selenium showed a brilliant surface; and only such selenium was employed, in order to get congruent results.

Selenium crystals of 3 millim. length were obtained by sublimation on the cover of the crucible. At first amorphous selenium condensed; afterwards these sublimated crystals, which were insoluble in water, were formed.

† Pogg. *Ann.* lxxxiv. p. 216.

‡ *Ann. Chim. et Phys.* (3) xlvi. p. 284.

for the explanation of the efficiency of the photophonic cells. (Here I will add that of course thermoelectric currents can be produced by differential heating of the two junctions. In order to get such a great difference of heating, the cell must be exposed to greater heat. Thus I brought near the focus of the sun's rays only one small part of the cell, and found a small deflection of 10 divisions, or about half a centimetre.)

That by radiation the allotropic modification of selenium may be changed, but that such changes do not occur in the selenium cells, was proved most conclusively by one piece of selenium, which had the anomalous property of showing increased resistance on being illuminated.

Till now I had prepared all selenium cells and all pieces of selenium as I have described above, in the open air or in an air-bath. I never succeeded in obtaining selenium pieces of such low resistance as Messrs. Adams and Day got in three of their pieces, the resistances of which were 55, 58, 68 ohms. These three pieces differ, it is true, strongly from most of the other pieces in their resistances, which were as high as 7,600,000 ohms. I therefore followed their method almost literally. I laid several pieces of amorphous selenium, furnished with platinum electrodes and wrapped in paper, for twenty-four hours in sand which had been warmed before by a red-hot iron ball,—a process in which the influence of the aqueous vapour evolved from the paper is not excluded. In this way I got, indeed, pieces of the comparatively low resistance of 700 and 2000 ohms; whilst that of the other pieces prepared at the same time amounted still to 350,000 ohms.

The selenium piece of lowest resistance (700 ohms) showed at first so variable a resistance, that this could scarcely be measured. Then, when it became more constant, a determination of 700 ohms was possible. But on exposure to light, the resistance *increased*. This behaviour is just the opposite of what all my other cells or pieces of selenium show. And it is equally in contradiction to the diminishing of resistance found in all other cases by all other observers; only Messrs. Adams and Day mention at the end of their numerous observations, that one single piece out of the great series behaved like this of mine, increasing its resistance on being illuminated. This piece of mine in which I observed this anomalous quality, exhibited in general the tendency to rise

steadily in resistance; so that there occurred, on illuminating it, a continuous increase of resistance, and, on darkening, a feeble but never a complete return to the original value. Every exposure to light again renewed this increase; and even a slight shaking of the table changed the resistance. This tendency to increase the resistance was manifested so strongly, that on the following day I found the resistance had risen from 700 to 5600 ohms.

But this piece of selenium showed still another anomaly, contributing, however, to the explanation of the first. I intended to examine the polarization produced in the selenium by the primary battery-current when separated from the battery and connected with the galvanometer by means of a switch. And now I found a secondary current which went through the galvanometer always in the same direction, quite independent of the direction of the primary battery-current. Even when the primary current was produced by a single Leclanché cell only, the deflection by the secondary current was 80 divisions, or about 5 centim. This secondary current is therefore no polarization-current; for in that case its direction would be always opposite to the primary. But here a change of direction did not occur, the secondary current always flowing from the platinum electrode A to the platinum electrode B, and never in the opposite direction.

The passage of a current also, like illumination or concussion, occasioned a quicker increase of resistance.

All these qualities, however, are very easily understood; and the very appearance of the piece suggests the explanation. There are in it several modifications of the selenium side by side. At the transformation of the one modification into another, as I have pointed out above, heat or electric effect must take place. A state of equilibrium is not reached before that modification has been formed the formation of which is attended by the maximum development of energy—thermal or electric. Such modification again, as also mentioned above, has a different resistance from the one from which it originated; and therefore the variation of resistance is a necessary consequence of the change of modification. While the transformation goes on, we observe the electric current; after the transformation is complete we observe the change of resistance.

Such changes in the modification can be also occasioned by light: a pencil of amorphous selenium assumes, when exposed to the daylight, a grey crystalline surface.

Two conditions distinguish these changes from the photophonic ones, and prove that, as a rule, they do not occur in the photophonic cells.

On darkening the cell in which only a microphonic action took action, the original state was reached again which it had before being illuminated; in the piece of selenium wherein a change of modification occurred, this was not the case. This is the reason why the light-spot returns to its original position on the galvanometer-scale in the case of the selenium cell, but does not in the case of the selenium piece. And, secondly, by such changes of modification a phenomenon is produced which has been called "fatigue." Such fatigue (that is, an insensitiveness) must take place as soon as the store of the one modification which is transforming itself into the other is exhausted. But it cannot take place if we have to deal with a microphonic action alone. And, indeed, in the selenium cells I never could observe this fatigue. The sensitiveness of the last-described piece is now extremely lowered.

And thus we see that there are two different effects which light may have on selenium and on selenium cells. The one is more of a chemical, the other more of a physical character. The one is a changing of modification, and is not essential to the efficiency of the selenium photophone. In this latter we have to deal essentially with a heating effect, changing volume and contact—in brief, with a microphonic action.

Therefore, as to the photophonic efficiency of selenium, I see no reason to separate it from all other bodies; and I no longer believe that there is any prospect of finding an unkown power or a new relation of forces in this substance.

The above experiments were performed in Prof. Guthrie's Physical Laboratory at the Science Schools, South Kensington. The permission granted me, at his request, by the Department of Science and Art to carry out my ideas experimentally is only one of the many acts of kindness and courtesy which I have received from scientific men and Societies during my sojourn in England.

Physical Laboratory, South Kensington,
June 1881.

XXXVII. *On Curves of Electromagnetic Induction.*

By W. GRANT*.

[Plates XV., XVI., & XVII.]

IN the month of June 1879 I communicated to the Physical Society a series of measurements of the conjugate positions of two equal circular coils† of wire whose axes were parallel to each other—that is to say, measurements of the relative positions of the coils when they were so placed that their coefficient of mutual induction became nothing. I also showed how, by the aid of these measurements, a curve could be drawn such that when one coil remained fixed, and the other was moved with its centre always in the curve and its axis parallel to that of the first coil, the mutual induction between the coils retained the constant value zero. An obvious extension of this investigation was to try to trace out some of the curves of constant positive or negative induction lying on opposite sides of the curve of no induction; and it is the results of experiments made for this purpose, along with those of others which were made for the purpose of tracing some of the curves of constant induction between the coils with their axes perpendicular to each other, which I have now to bring before the Society.

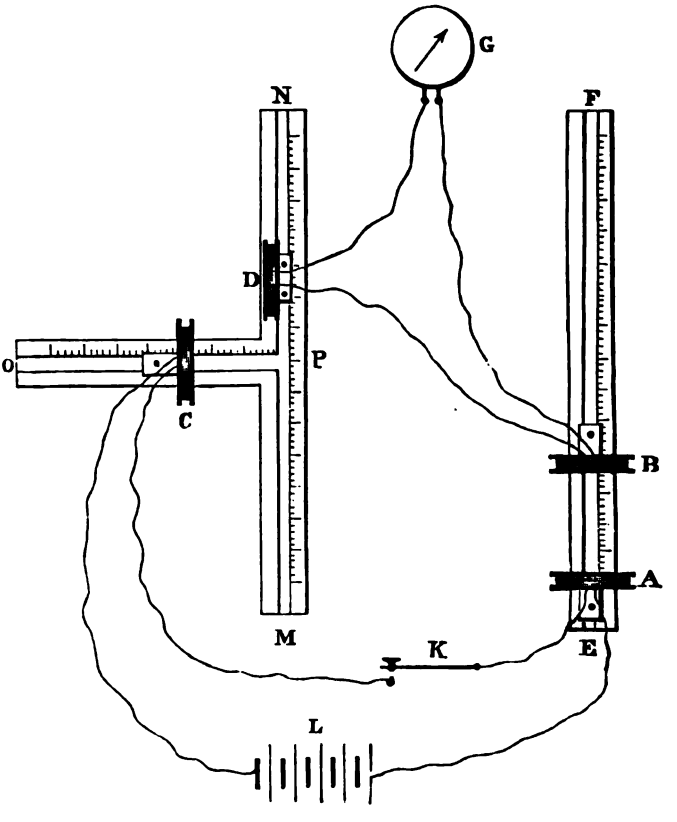
The arrangement of the apparatus and the nature of the experiments will be easily understood by reference to the annexed diagram.

A, B, C, and D are four coils of wire made as nearly identical in all respects as possible. Each coil consists of 182 turns of No. 24 silk-covered copper wire, of 0·065 centim. diameter, wound in a rectangular groove in a flat wooden reel. The inner circumferences of the coils are 21·95 centim.; their outer circumferences are 28·2 centim. The depth of the section of the coils perpendicular to the axis is 0·9947 centim.; the width of the groove parallel to the axis is 1·0 centim.: the section of the coils is therefore approximately one square centimetre. The mean radius is 3·99, or approximately 4·0

* Read June 11, 1881.

† Phil. Mag. for November, 1879.

centim. The resistances do not agree quite so closely; but their mean gives R=2·4 ohms at 11°·5 C.



The coils are mounted on straight guides which have grooves in their upper surfaces, along which the coils can be made to slide; and their positions are indicated by scales attached to the guides. The readings are obtained to centimetres and millimetres direct, and tenths of a millimetre by estimation. The coils A and B are mounted with their axes coincident on a straight guide E F, of sufficient length to allow their centres to be separated to a distance of 70 centimetres. The coils C and D are mounted on a pair of guides O P and M N, O P being about half the length of M N, and attached to it at right angles midway between its ends. The axes of the coils are parallel to O P and perpendicular to M N: hence

C can be moved parallel and D perpendicular to the axes without destroying the parallelism.

The coils A and C were connected with the battery L and with the key K to form the primary circuit; the coils B and D were connected with the galvanometer G, or sometimes with a telephone, to form the secondary circuit. Now it is evident that with this arrangement, in order that there may be no current in the secondary circuit on making and breaking the primary one, the coils C and D must be so placed that their mutual induction is equal to that between A and B; and, with reference to the secondary circuit, that the electromotive forces induced in the coils B and D must oppose each other. Hence, when A and B were clamped at a fixed distance apart, every pair of positions in which the coils C and D could be placed, so as not to cause a deflection of the galvanometer on making and breaking the primary circuit, were positions in which their mutual induction was constant, and determined one point of a curve of constant induction. Beginning with the coil D at P, the middle point of the guide M N, the coil C was moved until the induction between C and D balanced that between A and B. C was then moved nearer and nearer to P, being shifted a centimetre or so at a time; and the balance was restored in each case by moving D towards M or N. Now, as the arrangement is symmetrical with respect to the axis of C, it is evident that when a balance was obtained by displacing the coil D on one side of P, it could also be obtained by moving it to the corresponding position on the other side. In all cases these two balancing positions were found; and the half-difference of the readings on the scale M N, which was numbered from one end, was taken as the result of the experiment. In this way the measurements obtained were independent of any uncertainty in the determination of the point P. In using the numbers thus obtained for plotting a curve of constant induction, the distances read off along O P were taken as abscissæ, and the half-differences of the pairs of readings along M N were taken as ordinates. Thus in all the figures which accompany this paper, the axis of x is taken as coinciding with the axis of the primary coil with its centre fixed at the origin of coordinates, and the curves of constant induction are to be taken as representing

the paths traced out by the centre of the secondary coil in a plane containing the axes of x and y. The induced electromotive force changes sign when the centre of the secondary coil passes from one side to the other of the curve of no induction. In what follows, the induction is reckoned positive when the axes of the primary and secondary coils coincide. Hence, in the figures, all the curves lying between the axis of abscissæ and the zero-curve are to be taken as curves of positive induction; while those which lie further from the axis of abscissæ than the zero-curve are to be taken as curves of negative induction. The negative curves were traced experimentally in the same way as the positive curves, except that the two leading wires of one of the four coils were interchanged. Thus the inversion of electromotive force, due to the relative positions of the coils C and D, was counteracted by the inversion of the connections; and the inductive action between A and B could be balanced by that between C and D, just as in the measurements which gave the curves of positive induction.

The positive and negative divisions of the set of curves already alluded to, which, in what follows, are spoken of as the first set of curves, were each traced out with the apparatus arranged as in the diagram. But in order to trace out another set of curves, which are afterwards spoken of as the second set of curves, the axis of the coil D was set at right angles to that of C, but otherwise every thing remained unaltered. The zero-curve of the second set coincides with the axes of x and y; and therefore it did not require to be traced; each of the other curves is complete in one quadrant. The induced electromotive force changes sign when the centre of the coil D passes from one side to the other of the axes of x or of y: hence in the figures the second set of curves are to be taken as positive in one quadrant and negative in another alternately. The measurements for the second set of curves were made experimentally in the same way as for the first set; but as the axes of the coils C and D were at right angles, there was a considerable part of the field near the origin in which no measurements could be obtained, on account of the coils coming into contact with each other.

The positive or negative induction corresponding to any one

of the plotted curves being equal to that between A and B when placed at some definite distance from each other, it became necessary, in order to place the curves so that the numerical value of the induction-coefficient might have a known relative for each, to determine the law according to which the induction between the two coaxal coils A and B varied with the distance between them. For this purpose the coil A was connected with a contact-key and with a battery of 20 Grove's cells to form the primary circuit; the secondary circuit was formed by connecting the coil B with a contact-key and with the coils C and D, which were placed close together and used as a galvanometer. The needle and mirror employed were rather heavy: this had the advantage of allowing the induced currents to exert their full effect on the needle before it had moved perceptibly from its position of equilibrium. The key was a double-contact key, so arranged that on depressing the key the primary circuit was completed; and immediately afterwards, when the current was established, the secondary circuit, which was already complete, was opened, and was kept open by a spring acting on the lower key, while the primary circuit was then broken. The time occupied in depressing and releasing the key was in general about one third of a second; hence the time during which the primary current circulated every time that contact was made was approximately that period. With this arrangement only the induced current on making was allowed to act on the galvanometer, while that on breaking was prevented from circulating in the secondary circuit.

The temperature of the primary coil was indicated by a delicate thermometer divided to tenths of a degree Centigrade, which had its bulb placed in contact with the silk covering of the coil. The variation of the temperature of the coil, due to the heating effect of the current during the experiments (as indicated by this thermometer) was approximately 1°·0 C. The scale-readings obtained at the highest and lowest temperatures were found to agree so closely that it was unnecessary to make any correction on account of the variation of the temperature of the primary coil: its mean temperature during the experiments was 11°·5 C.

As the state of the battery was liable to change and the

strength of the current to vary, it was important that errors arising from these causes should as far as possible be eliminated. In order to effect this, a double set of observations was taken, first with increasing distances between the coils, and next with decreasing distances. In every position deflections were taken towards both ends of the scale; so that the recorded results represent the means of never less than four readings; and in most cases they are the means of twelve or sixteen. The observations were begun with the coils A and B as close together as possible without touching, and were continued till the distance between them was 70 centim.; but beyond about 50 centim. the galvanometer above mentioned, formed by the juxtaposition of the coils C and D, was not sufficiently sensitive. It was therefore replaced for these distances by a delicate reflecting galvanometer; and the necessary reduction was made after the ratio of the indications of the two instruments had been found. The deflections of the needle were indicated by the movements of a spot of light on a circular scale of one metre radius. The readings were obtained in centimetres and millimetres, and, after having been corrected for the effect of damping, were reduced to degrees. The value of the induced electromotive force, or, in other words, the strength of the induced current, was in each case taken as being proportional to the sine of half the angle through which the needle was deflected—that is, proportional to the sine of one fourth of the corrected scale-reading reduced to degrees. In using the numbers thus obtained for plotting a curve which graphically represents the values of the coefficient of mutual induction M for different distances of the coils A and B, the distances read off along the scale E F for the positions of the coil B were taken as abscissæ, and the values obtained for the sines were taken as ordinates. The results of these experiments are given in Table I., where the columns headed x give distances between the coils, and the columns z give the corresponding values of the coefficient of mutual induction. The curve plotted by means of these numbers is given in fig. 1, Plate XV.; the centres of the small circles in that and the following curves represent the points found in the experiments.

TABLE I.

Distance between centres of coils $=x$.	Relative value of induction-coefficient $=z$.	Distance between centres of coils $=x$.	Relative value of induction-coefficient $=z$.
centim.		centim.	
1·6	39·567	15·0	0·9
1·7	37·731	16·0	0·758
1·8	35·936	17·0	0·631
1·9	34·016	18·0	0·557
2·0	32·251	19·0	0·48
2·2	29·551	20·0	0·423
2·5	25·593	21·0	0·364
3·0	21·194	22·0	0·321
3·5	17·341	23·0	0·284
4·0	14·468	24·0	0·25
5·0	10·227	25·0	0·224
6·0	7·449	30·0	0·131
7·0	5·504	35·0	0·083
8·0	4·163	40·0	0·056
9·0	3·158	45·0	0·040
10·0	2·528	50·0	0·029
11·0	2·021	55·0	0·022
12·0	1·641	60·0	0·017
13·0	1·338	65·0	0·013
14·0	1·093	70·0	0·011

This curve is related to the curves of constant induction which form the main subject of this paper as the vertical section of a surface is related to the contour-lines of that surface. Imagine, then, a surface such that the three rectangular coordinates x, y, and z of any point upon it represent respectively the distance of that point from the centre of the primary coil, x being measured parallel to the axis of the coil, y perpendicular to it, and z being taken equal to M, the coefficient of mutual induction between the primary coil and the secondary coil placed with its centre at the point x, y, 0. Then, the curve just described may be viewed as a section of this surface in a plane containing the axes of x and z, the curves of constant induction may be looked upon as contour-lines of the surface, or as sections of it in planes parallel to the plane of x and y, and the curve whose coefficient of mutual induction is equal in value to z will pass through the point in question.

The values of M, whether positive or negative, are synonymous with those of z: hence in the figures the curves of variable induction, which are situated in vertical planes, are

to be taken as positive if they are above the plane of x and y, and negative if they are below it. Where the values of the coordinates of any curve are represented in the Tables by x and y, the curve is situated in a horizontal plane; where they are represented by x and z, the curve is situated in a vertical plane. On examining the numbers in this Table, it appears that the values of z or M are approximately inversely proportional to the cube of the distance from the centre of one coil to the mean circumference of the other—that is, that the product Mc^3 is approximately constant, c being put for $\sqrt{a^2+x^2}$, where a is the mean radius of one of the coils. On closer examination it is seen that this product decreases somewhat from $x=0$ to about $x=a$, and then slowly increases for greater values of x.

By means of the curve (fig. 1, Plate XV.) it was easy to place the coils A and B so that their coefficient of mutual induction might have any desired value within the available range, and thus to assign determinate relative values to the coefficients of mutual induction corresponding to the curves to be traced out by the coils C and D. In Table II. the *first* and *fourth* columns give reference numbers referring to the several curves plotted in fig. 2, Pl. XVI., whose coordinates are given in Table III.; the *third* and *sixth* give the corresponding values of M, the coefficient of mutual induction; and the *second* and *fifth* the distance along the scale E F at which the coils A and B had to be clamped in order to obtain these values.

TABLE II.

No. of curve.	x.	M.	No. of curve.	x.	M.
1	0·5	Uncertain.			
2	1·0	Uncertain.			
3	2·025	32·0	13	31·6	− 0·125
4	3·72	16·0	14	24·0	− 0·25
5	5·78	8·0	15	18·7	− 0·5
6	8·15	4·0	16	14·45	− 1·0
7	11·05	2·0	17	11·05	− 2·0
8	14·45	1·0	18	8·15	− 4·0
9	18·7	0·5	19	5·78	− 8·0
10	24·0	0·25	20	3·72	−16·0
11	31·6	0·125	21	2·025	−32·0
12	.....	Zero.			

The position on the scale E F, in which the coil B had to be placed in order to give the required value to the induction-coefficient of any curve, was found by inspecting Table II.; the coil was clamped in the position indicated; and a number of balancing pairs of positions of the coils C and D were then found.

In determining the values of the coordinates of the curve of zero induction the coils C and D only were employed. The primary circuit was the same as that in the diagram, omitting the coil A; the secondary circuit was also the same as that in the diagram, omitting the coil B. The coil C was brought as near as possible to the point P, and clamped in that position, sufficient room being left for the coil D to pass without touching it. D was then moved to a balancing position on one side of P, and then to the corresponding position on the other side of it, and the half-difference of the readings on the scale M N was taken as the value of the ordinate, the reading on the scale O P for the position of the coil C during the experiment being taken as the value of the corresponding abscissa.

The least distance between the centres of the coils C and D at which readings could be obtained when their axes were coincident was 1·6 centimetre, as their thickness prevented a nearer approach; the least distance between their axes at which readings could be obtained, when the mean planes of the coils were coincident or at a less distance than 1·6 centim. from each other, was about 9·2 centim. There was, therefore, in each quadrant a rectangular area of which these dimensions are the sides within which no results could be obtained.

In order to extend the experimental curves within this area, two coils, whose centres could be brought within 2 millim. of one another, were constructed from the remainder of the piece of wire from which the other four were made. Their diameters were approximately the same as those of the other coils; but, owing to their thinness and the consequent small number of convolutions of wire, their coefficient of mutual induction was much less; but this defect was compensated to some extent by their proximity. The lines of force due to them were slightly different in form from those due to the thick coils; but as in

most positions of the thin secondary coil the lines of force passed through it nearly at right angles, there was less objection to the use of the thin coils than if they had been at a greater distance apart. They were fitted one to each of the coils C and D, so that the same mountings served for both, and the readings were obtained from the same scales. That which was fitted to the former we shall call C_0, that which was fitted to the latter we shall call D_0.

In continuing the measurements within the area already mentioned, the coils C_0 and D_0 were placed in the same balancing pair of positions which C and D had occupied when the last point of a given positive curve was determined. The coil B was then moved towards F along the guide E F to a position in which the mutual induction between A and B balanced that between C_0 and D_0; this gave the desired value to the induction-coefficient of the curve; and the remaining points were found as in previous cases. Without again shifting the coil B, a negative curve, the induction-coefficient of which had the same relative value as that of the positive curve, could either be continued or completely traced out by interchanging the leading wires of the coil D_0 and passing it to the negative region. Thus the curves, whether positive or negative, could either be continued or completely traced out with the thin coils just as with the thick ones; and a constant value could be given to the mutual induction between the coils C_0 and D_0 in each pair of balancing positions, proportional to, although not the same as the value assigned to M for a given curve. Hence the path traced out by the centre of the coil D_0 was practically the same as that which would have been followed by the centre of the coil D, had it been possible to use it in tracing the same curve in that part of the field. The value of the induction-coefficient of each of the two curves nearest to the origin is uncertain, as the value of z which corresponds to that of x for either of these curves is beyond the range of the curve, fig. 1. A convenient, although uncertain value was given to the induction-coefficient of either of these curves by placing D_0 at the point P and moving C_0 towards O until the distance between the centres of C_0 and D_0 was equal to that between the origin and the point where the

curve was required to cross the axis of x, then balancing by the coil B and finding the remaining points of the curve. In completing several of these curves for which the value of M was comparatively small, it was found that the mutual induction between A and B was greater than that between C_0 and D_0, even when B was placed at the extreme end of the scale E F. Hence, in order to reduce it in such cases, B was laid down flat on the guide and displaced towards E or F until a balance was obtained; and although the value of the induction-coefficient was uncertain, the mutual induction between A and B was equal to that between C_0 and D_0 when they occupied a balancing pair of positions previously occupied by C and D, and remained constant while A and B retained the same relative positions.

The coordinates of the first set of curves of constant induction are given in Table III., and are numbered in accordance with Table II.

The results obtained by means of the thin coils C_0 and D_0 are distinguished in the Table by being enclosed in square brackets [ ].

Table III.

Curve 1, M uncertain.		Curve 2, M uncertain.	
x.	y.	x.	y.
[0·2]	[0·97]	[0·2]	[1·77]
[0·3]	[0·81]	[0·5]	[1·43]
[0·4]	[0·58]	[0·7]	[1·14]
[0·5]	[0·0]	[0·9]	[0·67]
		[1·0]	[0·0]
Curve 3, M = 32.		**Curve 4, M = 16.**	
[0·2]	[3·06]	[0·2]	[4·35]
[1·0]	[2·4]	[1·0]	[4·07]
1·6	1·59	1·6	3·74
1·9	0·88	2·0	3·46
2·025	0·0	3·0	2·37
		3·5	1·35
		3·72	0·0
Curve 5, M = 8.		**Curve 6, M = 4.**	
[0·2]	[5·17]	[0·2]	[5·65]
[1·0]	[5·07]	[1·0]	[5·69]
1·6	4·985	1·6	5·695
2·0	4·885	2·0	5·705
3·0	4·505	3·0	5·68
4·0	3·855	4·0	5·5
5·0	2·705	5·0	5·15
5·5	1·66	6·0	4·53
5·78	0·0	7·0	3·5
		7·5	2·69
		8·0	1·345
		8·15	0·0
Curve 7, M = 2.		**Curve 8, M = 1.**	
[0·2]	[5·89]	[0·2]	[6·0]
[1·0]	[6·0]	[1·0]	[6·15]
1·6	6·105	1·6	6·325
2·0	6·195	2·0	6·475
3·0	6·43	3·0	6·89
4·0	6·585	4·0	7·28
6·0	6·495	6·0	7·84
8·0	5·69	8·0	7·84
9·0	4·935	10·0	7·25
10·0	3·685	12·0	5·925
10·5	2·73	13·0	4·685
10·8	1·8	14·0	2·885
11·05	0·0	14·3	1·555
		14·45	0·0

Table III. (*continued*).

Curve 9, M=0·5.		Curve 10, M=0·25.	
x.	*y*.	*x*.	*y*.
[0·2]	[6·07]	[0·2]	[6·12]
[1·0]	[6·24]	[1·0]	[6·29]
1·6	6·445	1·6	6·515
2·0	6·63	2·0	6·715
3·0	7·18	3·0	7·325
4·0	7·745	4·0	8·04
6·0	8·79	6·0	9·475
8·0	9·435	8·0	10·66
10·0	9·61	10·0	11·465
12·0	9·33	12·0	11·845
14·0	8·455	14·0	11·825
16·0	6·845	16·0	11·45
17·0	5·55	18·0	10·56
18·0	3·49	19·0	9·9
18·5	1·8	20·0	9·05
18·7	0·0	21·0	8·05
		22·0	6·775
		23·0	4·85
		23·5	3·2
		23·8	1·74
		24·0	0·0
Curve 11, M=0·125.			
[0·2]	[6·14]	20·0	15·0
[1·0]	[6·32]	22·0	14·45
1·6	6·545	24·0	13·55
2·0	6·76	25·5	12·525
3·0	7·42	27·0	11·175
4·0	8·215	28·0	10·05
6·0	9·965	29·0	8·725
8·0	11·635	30·0	6·83
10·0	13·025	30·5	5·5
12·0	14·075	31·0	3·95
14·0	14·82	31·4	2·05
16·0	15·2	31·6	0·0
18·0	15·2		
Curve 12, M=zero.			
[0·2]	[6·15]	12·0	18·055
[1·0]	[6·35]	13·0	19·45
1·6	6·575	14·0	20·775
2·0	6·8	15·0	22·15
2·5	7·135	16·0	23·54
3·0	7·5	17·0	24·9
4·0	8·38	18·0	26·275
5·0	9·395	19·0	27·65
6·0	10·505	20·0	29·0
7·0	11·675	21·0	30·376
8·0	12·89	22·0	31·775
9·0	14·115	23·0	33·13
10·0	15·4	24·0	34·5
11·0	16·745		

Table III. (*continued*).

Curve 13, M = −0·125.			Curve 14, M = −0·25.		
x.	*y*.	*y'*.	*x*.	*y*.	*y'*.
0	.....	26·0	0	.....	20·22
[0·2]	[6·16]	.....	[0·2]	[6·18]	.....
[1·0]	[6·38]	25·97	[1·0]	[6·42]	20·105
1·6	6·615	25·86	1·6	6·64	19·97
2·0	6·845	25·81	2·0	6·89	19·83
3·0	7·6	25·5	3·0	7·72	19·35
4·0	8·58	25·0	4·0	8·855	18·56
5·0	9·795	24·35	5·0	10·475	17·365
6·0	11·275	23·4	5·7	12·4	15·75
7·0	13·33	21·95	5·9	14·05	14·05
7·7	15·325	19·95			
8·0	18·05	18·05			

Curve 15, M = −0·5.			Curve 16, M = −1·0.		
0	.....	16·27	0	.....	13·305
[0·2]	[6·2]	.....	[0·2]	[6·24]	.....
[1·0]	[6·48]	16·21	[1·0]	[6·56]	13·125
1·6	6·725	15·975	1·6	6·865	12·85
2·0	7·0	15·79	2·0	7·195	12·6
3·0	7·96	15·09	3·0	8·73	11·27
4·0	9·62	13·74	3·2	9·49	10·605
4·4	11·9	12·33			

Curve 17, M = −2·0.			Curve 18, M = −4·0.		
0	.....	11·085	0	.....	9·445
[0·2]	[6·35]	.....	[0·2]	[6·64]	.....
[1·0]	[6·7]	10·835	[0·5]	[6·81]	9·33
1·6	7·215	10·4	[0·7]	[7·02]	9·225
2·0	7·825	9·845	[1·0]	[7·445]	[8·85]
2·2	8·48	9·18	[1·2]	[8·15]	[8·15]

Curve 19, M = −8·0.			Curve 20, M = −16·0.		
[0·2]	[7·165]	[8·42]	**0**	**7·45**	**8·0**
[0·3]	[7.33]	[8·29]	**0·1**	**7·52**	**7·95**
[0·4]	[7·6]	[8·02]	**0·15**	**7·7**	**7·83**

Point of maximum negative intensity, No. 21, M = −32·0.	
x.	*y*.
0	**7·7**

The first set of curves of constant induction are given in fig. 2, Plate XVI. Curve 20 and the point of maximum negative induction could not be found experimentally; they are therefore only given as near approximations. The rectangular space near the origin shows the region within which the auxiliary coils C_0 and D_0 (see p. 369) had to be employed. These curves represent the contour-lines of one quadrant of the surface above described, and show at what distance from the origin any curve cuts the axis of y. Knowing this, and knowing also the relative value of M or of z for each curve, we obtain a set of values for the coordinates of a curve which may be viewed as a section of the surface in question in a plane containing the axes of y and z. These coordinates are given in Table IV.; the curve plotted by means of them is given in fig. 3, Pl. XVII.; but the dotted part of it is only approximate.

TABLE IV.

y.	x.	y.	y'.	x.
2·6	39·55	6·15	26·0	− 0·125
3·07	32·0	6·17	20·22	− 0·25
4·38	16·0	6·19	16·27	− 0·5
5·18	8·0	6·23	13·305	− 1·0
5·64	4·0	6·33	11·085	− 2·0
5·88	2·0	6·58	9·44	− 4·0
5·99	1·0	7·02	8·48	− 8·0
6·06	0·5	7·45	8·0	−16·0
6·11	0·25	7·7	7·7	−32·0
6·13	0·125			
6·14	0·0			

In order to give a better idea of the symmetry of the curves of constant induction than can be got from fig. 2, the curves in that figure have been repeated in the other quadrants, and are given in fig. 4, Pl. XVII., for the whole of the magnetic field of the primary coil. Now every thing is symmetrical relatively to the axis of x, and each curve represents a section of a surface of revolution about that axis. Hence, if the curves are supposed to revolve round the axis of x, a number of surfaces of revolution will be generated, each of which will be a surface of constant induction, the surfaces of positive induction being separated from those of negative induction by the surface of no induction. The positive surfaces may be described as shells which enclose one another, and each of which turns inwards, closing up round the axis of x on each side of the origin. The zero-surface, which divides the positive from the

negative surfaces, instead of closing up, may be supposed to extend in space to an infinite distance. The negative surfaces turn outwards and close up in a plane containing the axes of x and z; they are hollow circular rings which enclose one another, and which have their common centre at the origin of coordinates.

In the series of measurements for the determination of the second set of curves, the axis of the coil D was perpendicular to that of C, but otherwise every thing was arranged as in the diagram. The same values were given to M for these curves as for the others, by setting the coil B in the same positions on the scale E F which it had occupied during the previous experiments. These curves are numbered in accordance with Table V.

TABLE V.

Number of curve.	x.	M.
1	31·6	0·125
2	24·0	0·25
3	18·7	0·5
4	14·45	1·0
5	11·05	2·0
6	8·15	4·0

The zero-curve of this set coincides with the axes of coordinates; and, in general, when two similar coils with their axes perpendicular are employed, one as primary and the other as secondary, their mutual induction is zero when the axis of the one lies in the mean plane of the other. This shows that any curve of the second set for which the value of M is small must make a near approach to the axes of coordinates in the neighbourhood of the origin, and that a part of each curve in that region cannot be traced experimentally with the coils employed. The coordinates of these curves, as far as it was found possible to determine them experimentally, are given in Table VI.; but there is with this set a larger space near the origin within which the dimensions of the coils made it impossible to get measurements than was the case with the first set of curves. In the figures, the curves are continued conjecturally within this space by dotted lines. The second set of curves are given in fig. 5, Pl. XVI.

TABLE VI.

Curve 1, M=0·125.					
x.	*y.*	*y'.*	*x.*	*y.*	*y'.*
0·06	.....	5·02	5·5	0·05	21·88
0·1	.....	7·1	6·0	0·05	22·22
0·2	.....	9·26	8·0	0·12	23·3
0·3	.....	10·45	10·0	0·23	23·85
0·4	.....	11·34	12·0	0·47	24·15
0·5	.....	12·1	14·0	0·84	23·97
0·7	.....	13·3	16·0	1·35	23·49
1·0	.....	14·54	18·0	2·3	22·57
1·5	.....	16·2	20·0	3·67	21·1
2·0	.....	17·37	22·0	5·72	18·9
3·0	.....	19·18	23·0	7·29	17·05
4·0	.....	20·48	24·0	10·25	13·48
5·0	.....	21·42			

Curve 2, M=0·25.					
x.	*y.*	*y'.*	*x.*	*y.*	*y'.*
0·1	.....	5·09	5·0	.....	17·26
0·2	.....	7·18	5·5	0·1	17·54
0·3	.....	8·28	6·0	0·11	17·77
0·4	.....	9·16	8·0	0·24	18·36
0·5	.....	9·77	10·0	0·53	18·45
0·7	.....	10·74	12·0	1·03	18·02
1·0	.....	11·82	14·0	1·9	17·1
1·5	.....	13·13	16·0	3·44	15·45
2·0	.....	14·13	17·0	4·55	14·22
3·0	.....	15·55	18·0	6·51	12·27
4·0	.....	16·54	18·4	8·0	10·4

Curve 3, M=0·5.			Curve 4, M=1·0.		
x.	*y.*	*y'.*	*x.*	*y.*	*y'.*
0·21	.....	5·4	0·4	.....	5·42
0·3	.....	6·4	0·5	.....	6·1
0·4	.....	7·24	0·7	.....	7·02
0·5	.....	7·84	1·0	.....	7·92
0·7	.....	8·72	1·5	.....	8·89
1·0	.....	9·72	2·0	.....	9·57
1·5	.....	10·88	3·0	.....	10·52
2·0	.....	11·65	4·0	.....	11·06
3·0	.....	12·82	5·5	0·39	.....
4·0	.....	13·59	6·0	0·46	11·46
5·0	0·17	14·1	8·0	1·01	11·04
5·5	0·19	14·28	10·0	2·33	9·64
6·0	0·23	14·38	11·0	3·85	8·11
8·0	0·5	14·54	11·4	5·0	6·9
10·0	1·07	14·06			
12·0	2·19	12·87			
13·0	3·17	11·82			
14·0	4·69	10·17			
14·5	6·34	8·35			

Table VI. (*continued*).

Curve 5, M=2.			Curve 6, M=4.		
x.	*y*.	*y'*.	*x*.	*y*.	*y'*.
0·8	.....	5·54	1·6	.....	5·5
1·0	.....	6·17	1·8	.....	5·76
1·6	.....	7·27	2·0	.....	6·0
2·0	.....	7·76	2·5	.....	6·45
3·0	.....	8·54	3·0	.....	6·72
4·0	.....	8·91	4·0	.....	6·96
5·0	.....	9·0	5·0	.....	6·82
5·2	0·69	.....	5·5	1·55	6·66
6·0	0·92	8·85	6·0	1·9	6·31
7·0	1·37	8·41	6·5	2·45	5·78
8·0	2·23	7·58	7·0	3·62	4·61
9·0	4·13	5·56			

The positive and negative curves of the second set have the same form, and are positive in one quadrant and negative in another alternately. They have been treated as an independent set of curves; but, as will afterwards appear, they are not so, but are merely a special case in which the positive curves of the first set have become separated by the intervening zero-curve which coincides with the axes of x and y. In this case any corresponding pair of positive and negative curves, besides having the same form, have also the same linear dimensions. In every other case the form and linear dimensions of any corresponding pair of positive and negative curves are different, the linear dimension of the negative curve being always less than that of the positive. Hence this is the case in which the linear dimension of any negative curve is greatest, and in which that of the corresponding positive curve is least. The second set of curves, for the whole of the magnetic field, are given in fig. 6, Pl. XV., which shows the relative positions occupied by them in the various quadrants.

When a system of curves of constant induction have been obtained for a given pair of coils, they may be used to give the total inductive effect produced on one of the coils by a given change of relative position while the other coil is traversed by a current of known strength. To simplify the statement, suppose the primary coil in which there is a current of uniform strength C to remain at rest while the secondary coil is moved from a position such that the coefficient of mutual

induction is M_1, to a position in which this coefficient becomes M_2. Then, if t is the time occupied by the movement, the average electromotive force e which acts in the secondary circuit during the movement is

$$e=\frac{M_2-M_1}{t}C;$$

and if r be the resistance of the secondary circuit, the average strength of the secondary current is

$$c=\frac{e}{r}=\frac{M_2-M_1}{rt}C.$$

The total quantity, q, of electricity conveyed by the secondary current is consequently

$$q=ct=\frac{M_2-M_1}{r}C,$$

and is therefore independent of the time occupied in the displacement of the secondary coil.

The values of M_1 and M_2, the coefficients of induction corresponding to the initial and final positions of the secondary coil, can be obtained by inspection of diagrams of curves of constant induction such as those which accompany this paper. It is evident that the total secondary current is nothing in every case in which the secondary coil is moved so as to make $M_2=M_1$ (that is, whenever the secondary coil in its final position is on the same curve as in its first position), and that the secondary current is positive when the absolute value of M_2 is greater than that of M_1, and negative when M_2 is less than M_1.

The spaces between the curves in the figures may be filled up as follows by other curves, for which the values of M lie within the available range of the curve fig. 1. Assume a value for M which will lie between its values for two curves already drawn; take this as the value of z, and find the point of the curve fig. 1 to which it corresponds. A point on the axis of x will thus be found, which will divide the distance between the two points on that axis, whose values are those of x for the given curves, into two parts whose ratio may easily be found. Then, if a series of points between the two given curves are found for which this ratio is constant, a curve joining these points will be a curve of constant induction, for which the value of M will be that which was assumed.

The curves of constant induction may also be employed in a graphic method for determining, at a number of points in the magnetic field, the direction of the resultant inductive effect on the secondary coil in the positions in which it was used in the measurements for determining the two sets of curves. If the curves figs. 2 and 5 are superposed as in fig. 7, Pl. XVI., we may resolve by the parallelogram of forces at a number of points where the curves intersect. For this purpose components are taken whose values are proportional to the values of M for the curves, and, from the point where any two curves intersect, lines are drawn proportional to these values for the two intersecting curves. The component which is proportional to the value of M for the curve of the first set is drawn parallel to the axis of x; and that for the curve of the second set is drawn at right angles to it. Compounding, we then obtain as resultant a straight line proportional to the magnitude, and in the direction, of the resultant inductive effect on the secondary coil in two positions at right angles to each other. The arrows at the points of intersection of the curves in fig. 7 show the directions of these resultants. If the curves had been obtained by means of an indefinitely small secondary coil, the resultants would have been tangents to the lines of force, and the straight lines drawn through the same points at right angles to the resultants would have been tangents to the equipotential curves; but with the coils employed this is not strictly the case.

The two sets of curves in the figures are so related to one another that the one set may be viewed as a modified form of the other. If we begin with the axes of the primary and secondary coils parallel, and gradually increase the angle between them, the curves of maximum induction, as it were, carry the curves of constant induction round with them, while the curves of zero induction, in moving round, always form lines of demarcation which separate the positive from the negative regions. The positive curves of constant induction at the same time become distorted and gradually contract, the linear dimensions of each curve becoming less until the angle between the axes is about 90°. When this angle has become exactly 90°, the positive curves of constant induction have become separated into two distinct divisions by the intervening zero-curve (which coincides with the axes

of x and y), so that they then occupy two opposite quadrants. Now, both the positive and the negative curves move round together; but as the negative curves are carried round they become distorted and gradually expand, the linear dimensions of each curve becoming greater until the angle between the axes of the coils is 90°. When this, which is the extreme or limiting case, has been reached, the form and linear dimensions of any negative curve are the same as those of either of the two corresponding positive curves for which the value of M is the same, and the two sets of negative curves, which originally were each bisected by the axis of y, have then come to occupy the two remaining opposite quadrants. Thus the one set of curves of constant induction merges into the other, and the forms of both sets, which may be described as ovals, depend upon the angle between the axes of the primary and secondary coils.

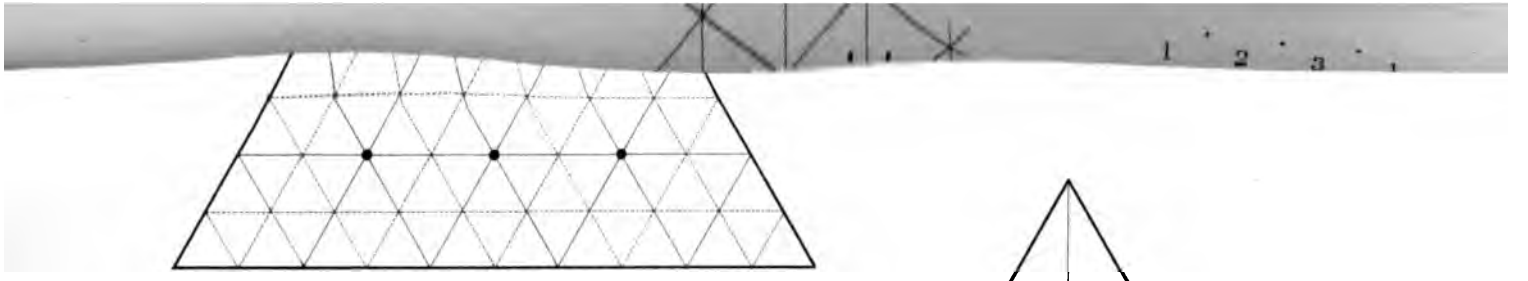
We see, then, that the second set of curves, although found experimentally, are not entirely independent of the first set, and that being positive and negative in alternate quadrants, they have no corresponding surfaces of revolution, that the only curves of constant induction which have corresponding surfaces of revolution are those which are obtained when the axes of the primary and secondary coils are parallel, and that all curves of constant induction which are due to the coils when their axes make any other angle with each other are merely modified forms of them.

The arrangement of apparatus employed in this investigation, namely two similar coils in the primary and two other similar coils in the secondary circuit, was employed by Dove in his researches, and was called by him the "Differential Inductor" (*Annales de Chimie et de Physique*, tome iv. 1842).

The same arrangement was employed by Felici, a short account of whose researches is given in Maxwell's 'Electricity and Magnetism,' vol. ii. pp. 169–172.

In conclusion, my special thanks are due to Prof. G. C. Foster, for the general interest which he has taken in this subject, and for many important suggestions made during the progress of the investigation.





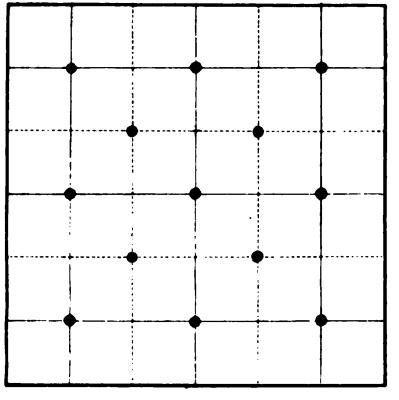


Fig. 7.

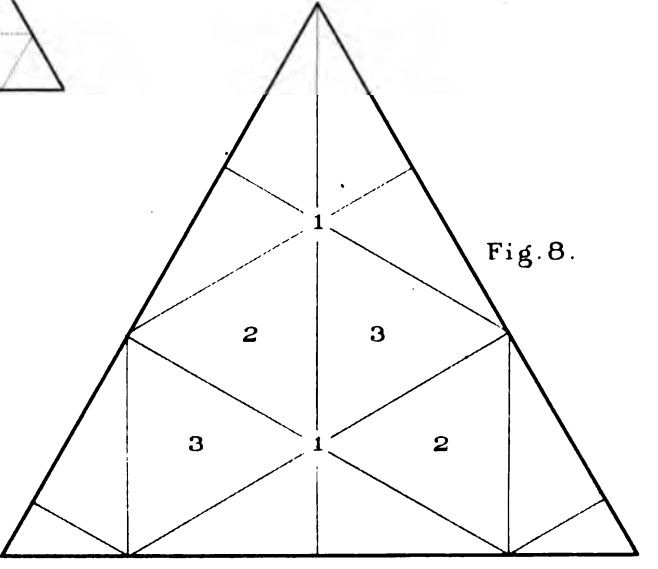
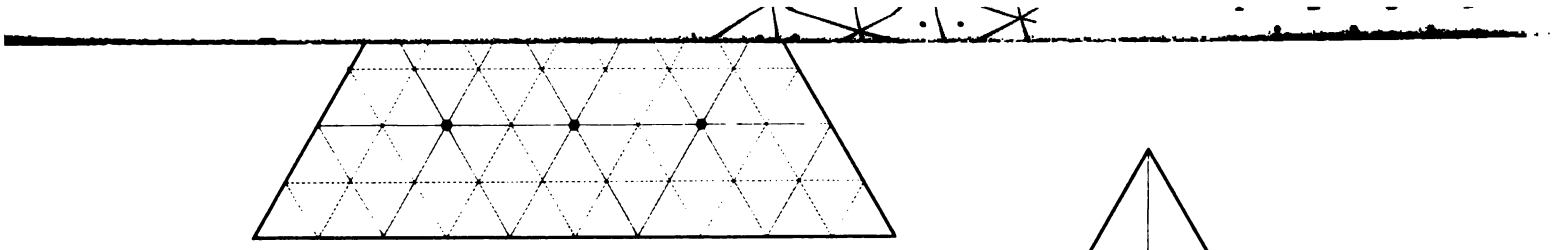


Fig. 8.

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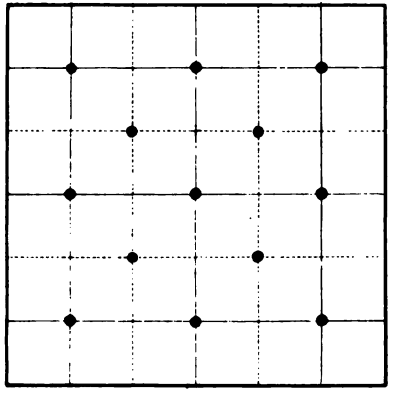


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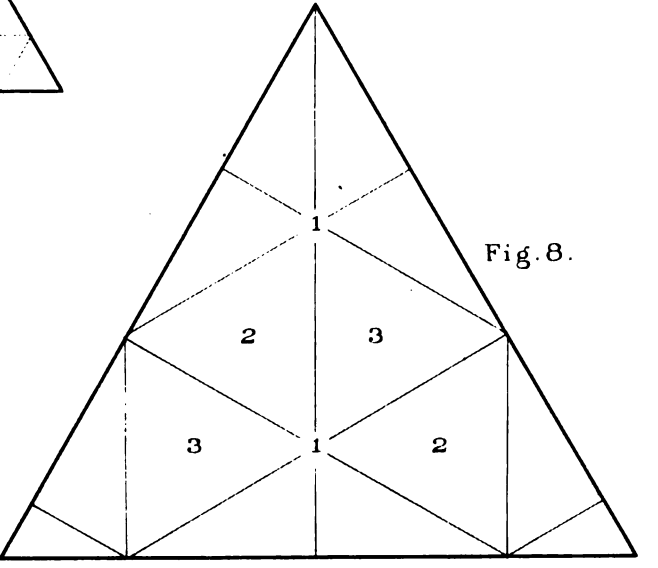
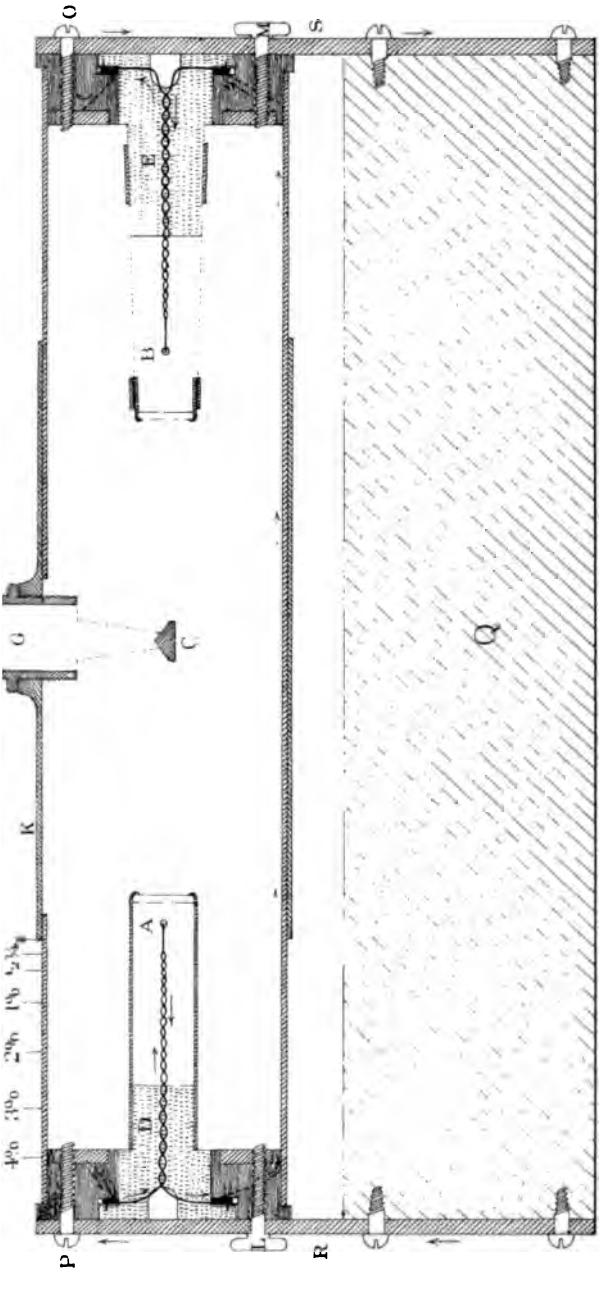


Fig. 8.

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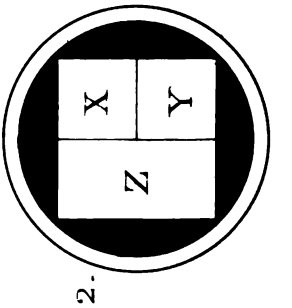


Fig. 2.

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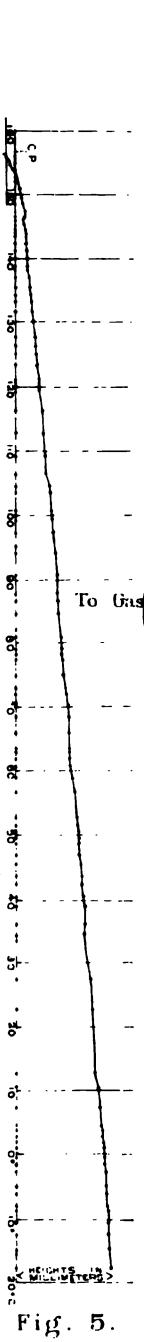


Fig. 5.

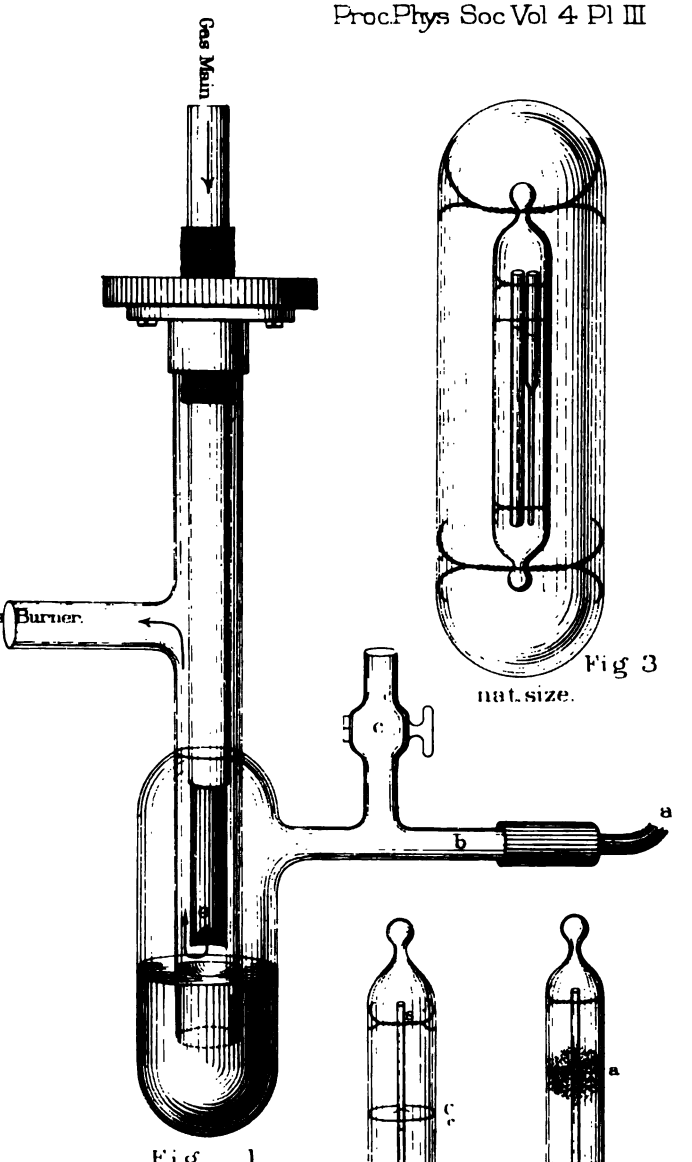


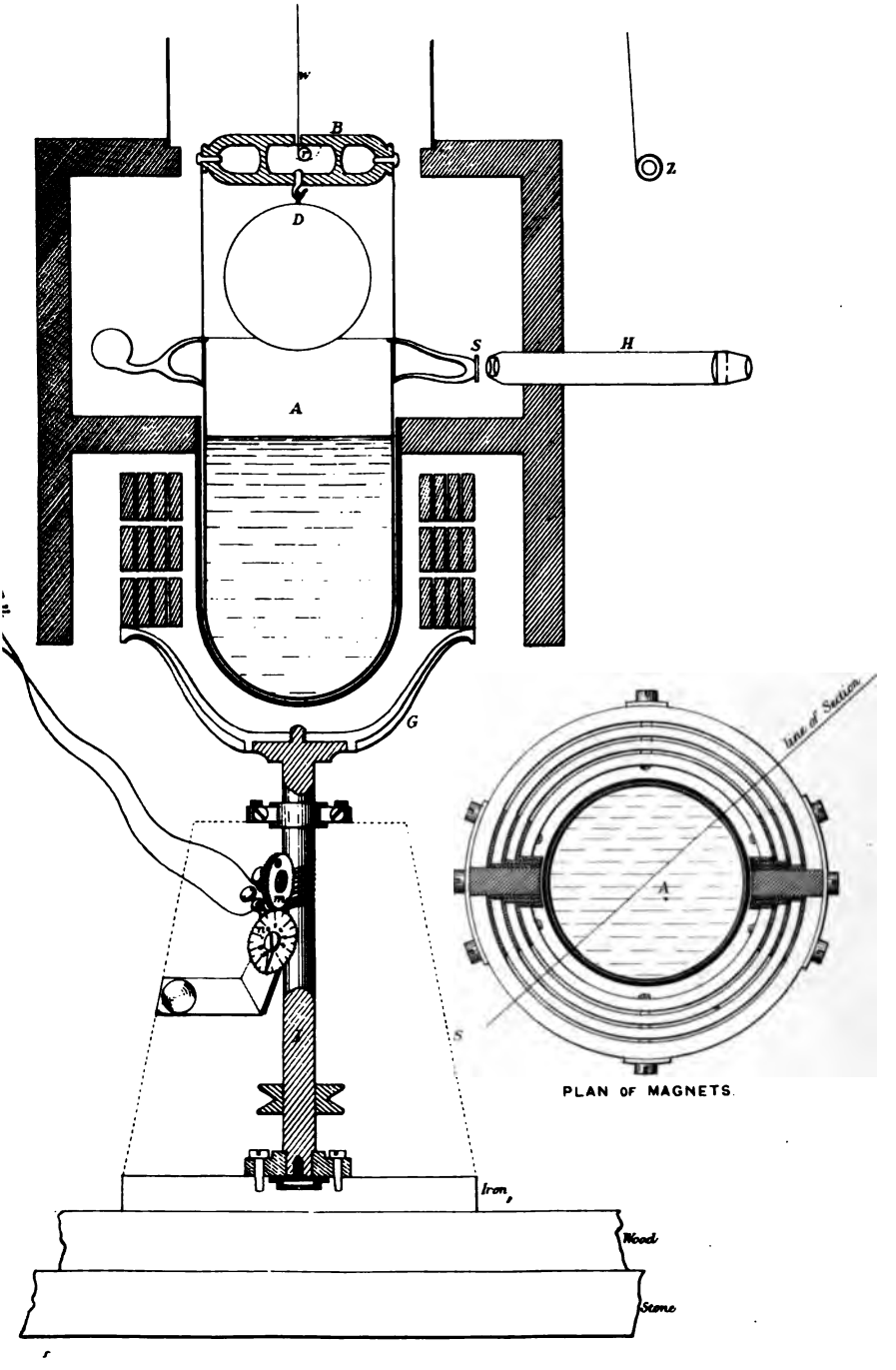
Fig. 1.
Scale $\frac{1}{3}$.

Fig 3
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Fig. 2.
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Fig. 4.
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Mintern Bros lith



Mintern Bros. lith.

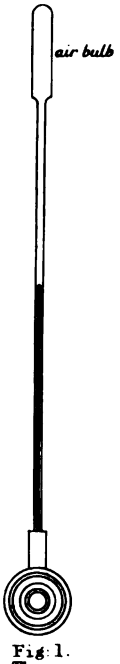


Fig: 1.
Air Thermometer

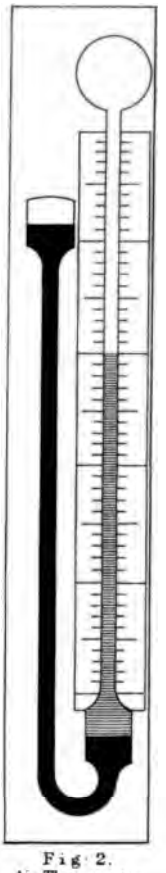


Fig: 2.
Air Thermometer.

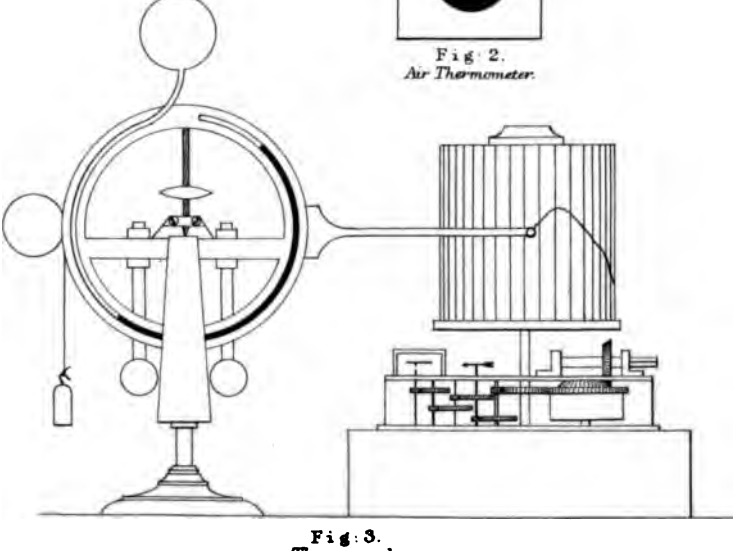


Fig: 3.
Thermograph.

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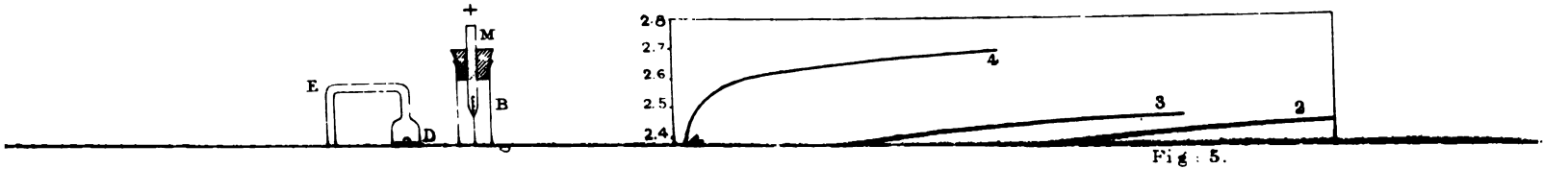

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Fig: 5.

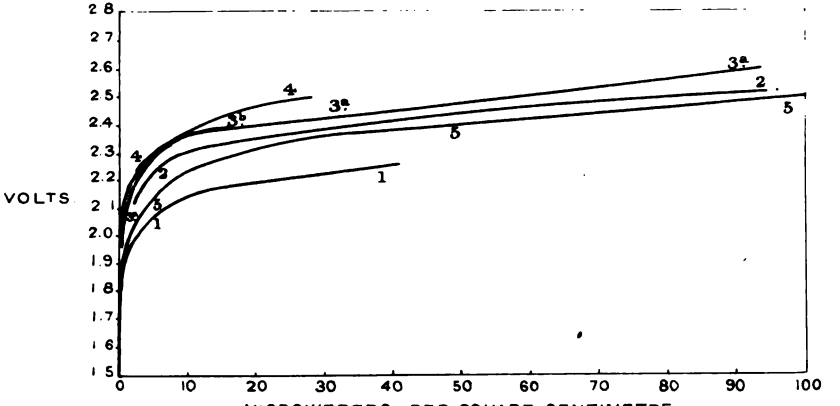

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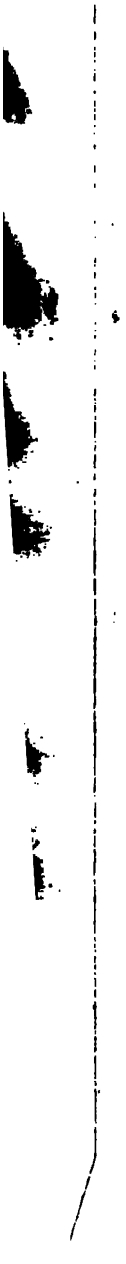
Fig: 4.





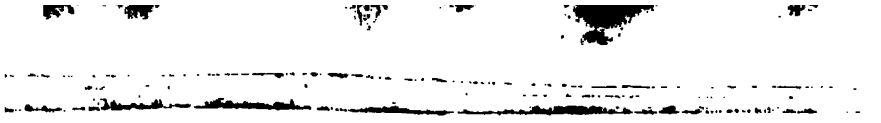












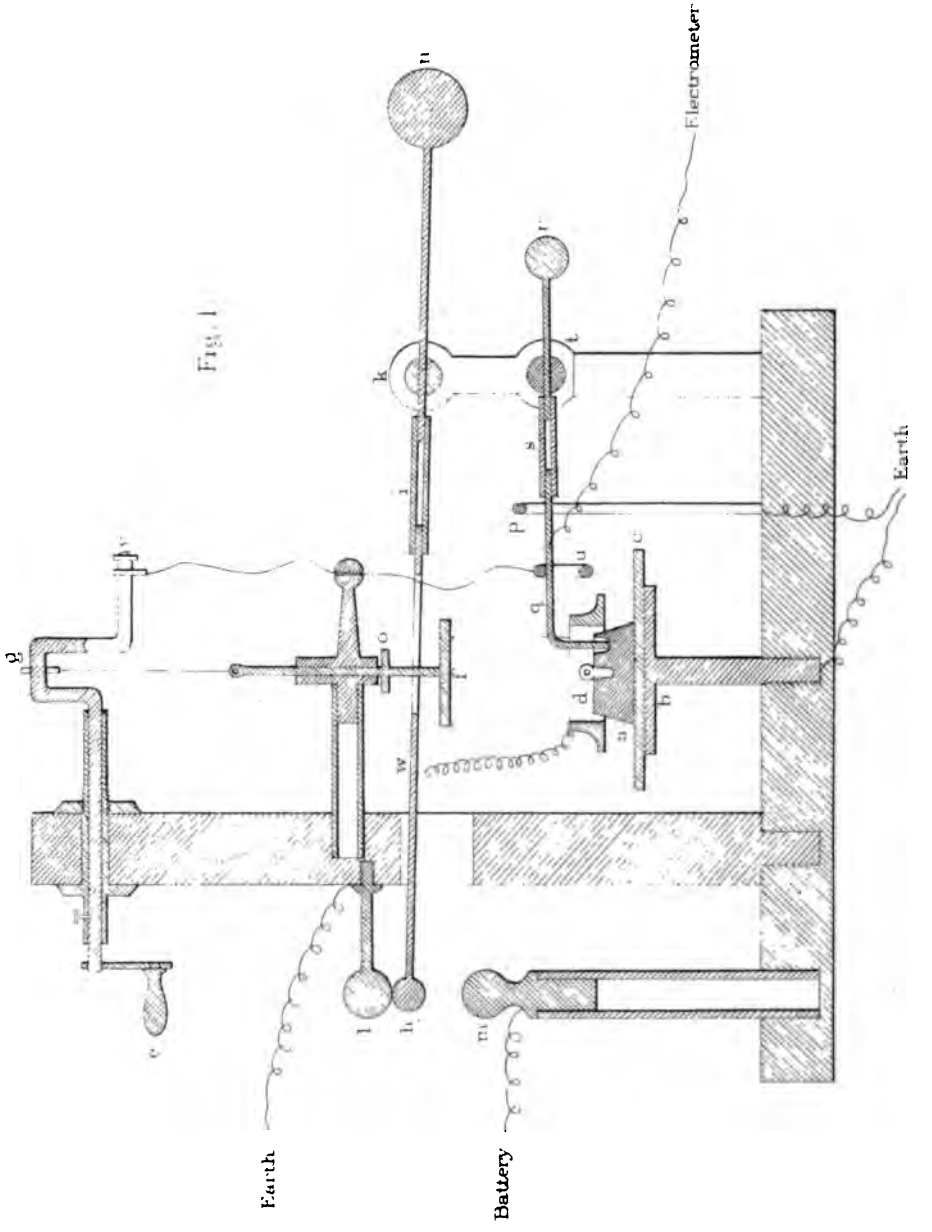


Fig. 1.

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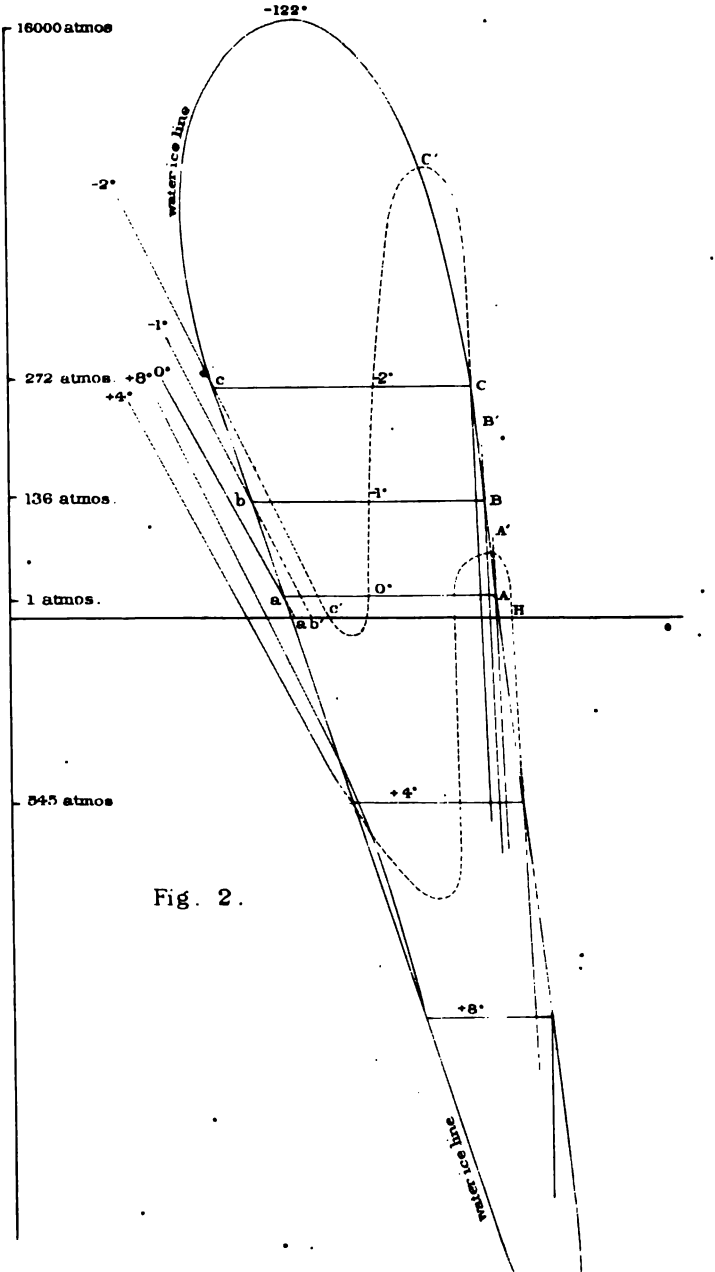


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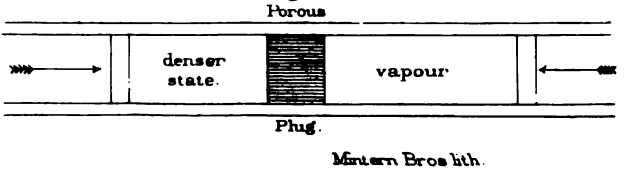


Fig. 1.

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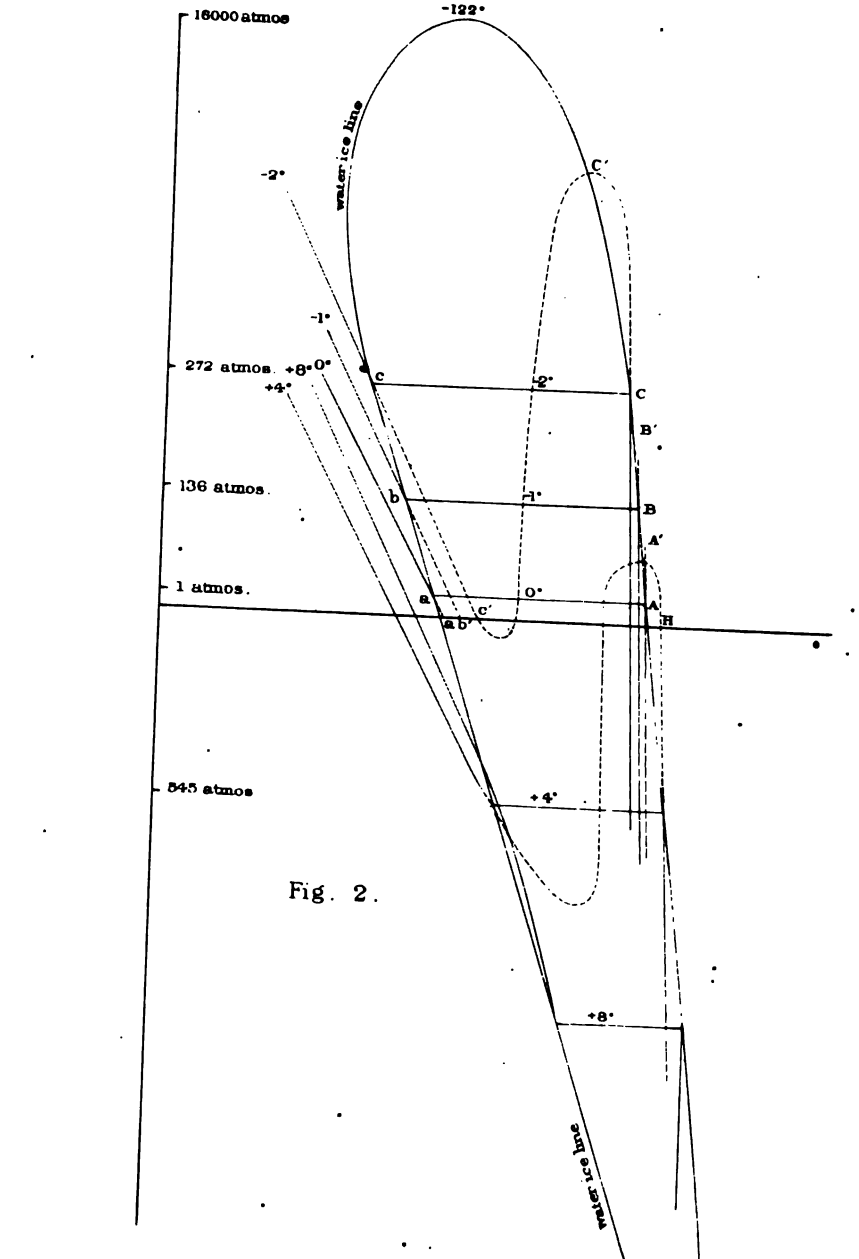


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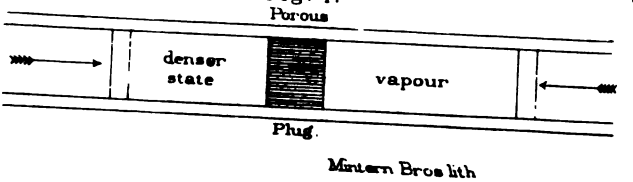
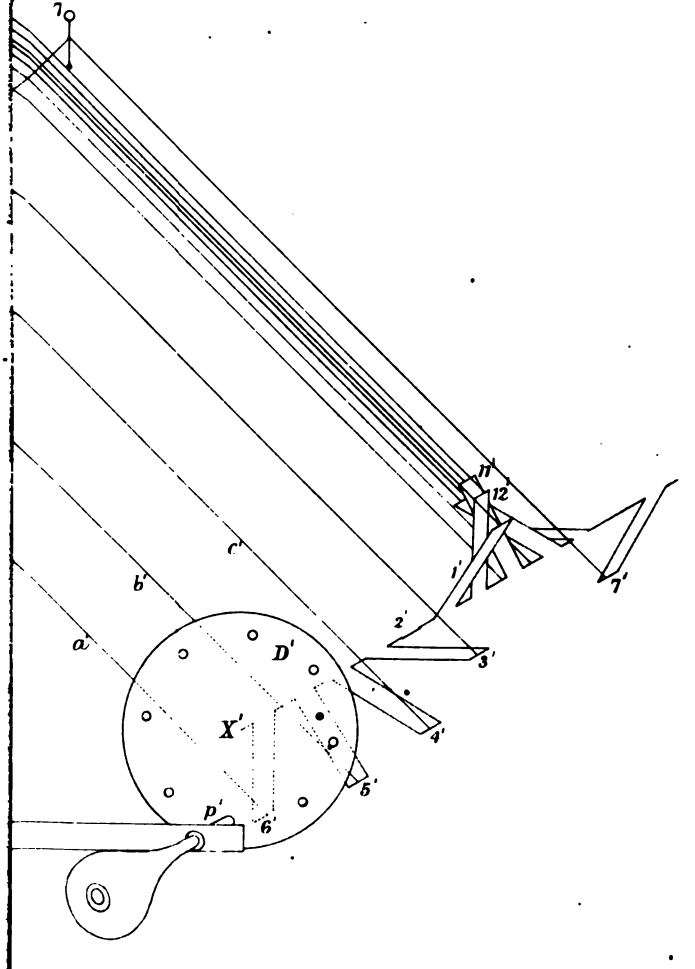


Fig. 1.

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p'
6'



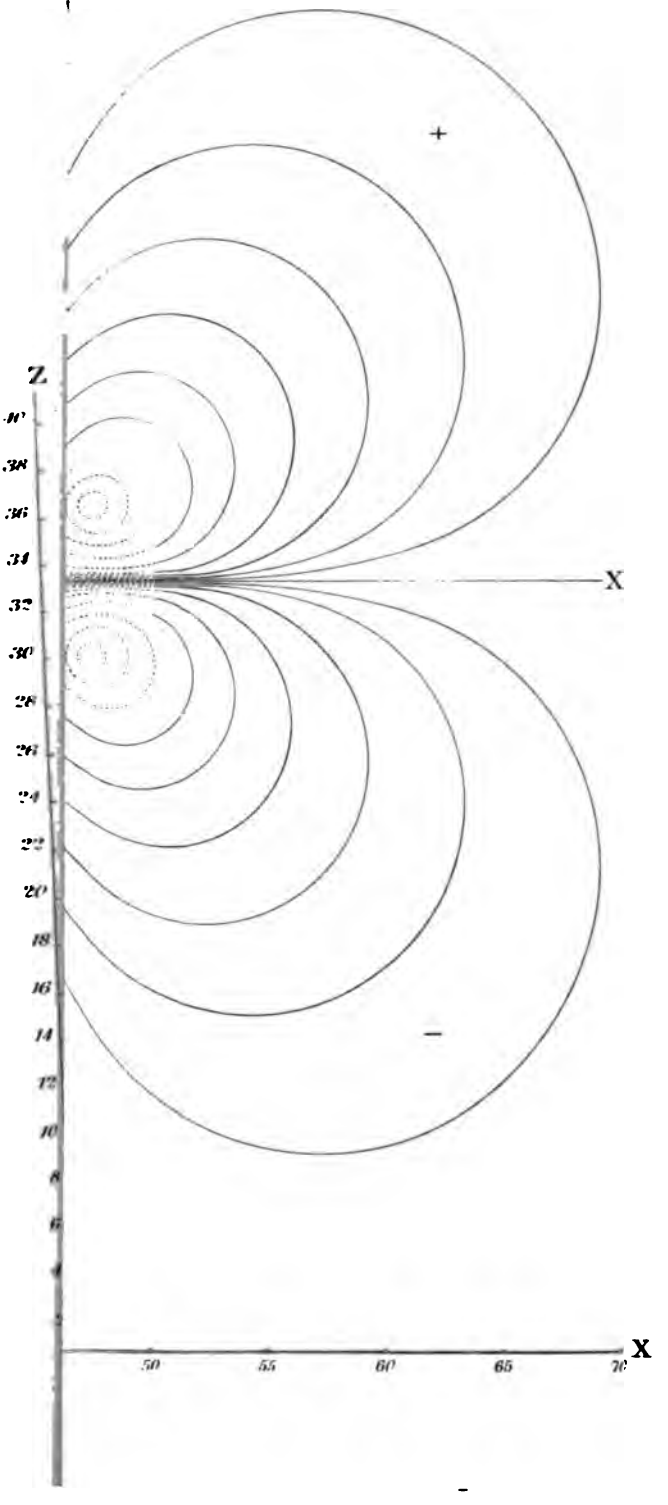

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Fig. 2.

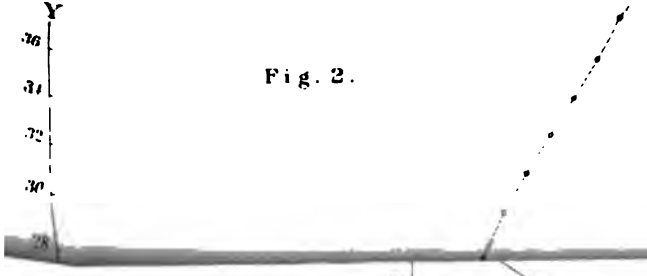
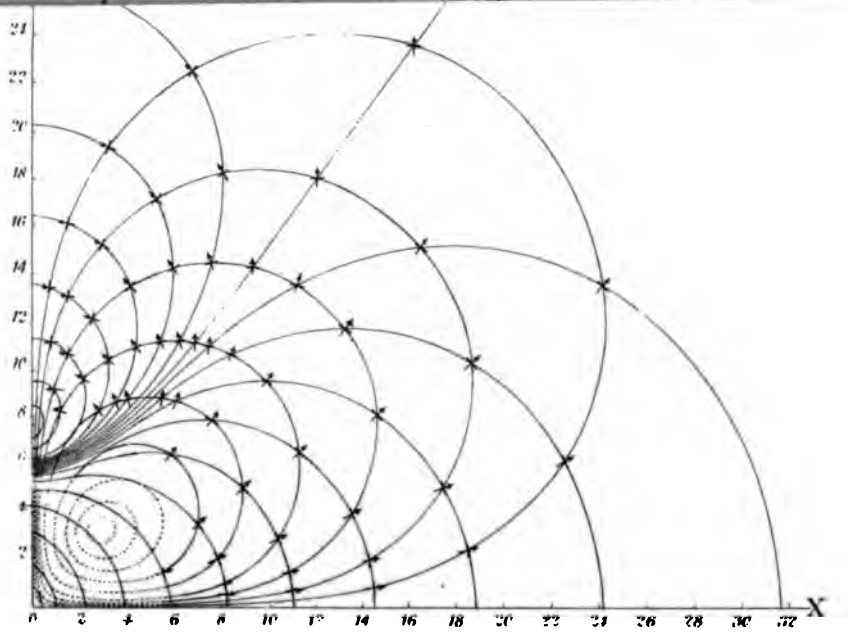


Fig. 5.



Mintern Bros lith.



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PROCEEDINGS

AT THE

MEETINGS OF THE PHYSICAL SOCIETY

OF LONDON.

SESSION 1880-81.

February 14th, 1880.

Prof. W. G. Adams, M.A., F.R.S., Vice-President, in the Chair.

The following were elected Members of the Society:—

A. Mollison, M.A.; T. C. Lewis, M.A.; Señor Dr. Rafael Roig y Torres; A. T. Hare, B.A.; Miss Caroline A. Martineau.

The following papers were read:—

"On a Spectroscope with Telescope and Collimator Lenses achromatized by Quartz and Iceland Spar." By Dr. W. H. Stone.

"On an Automatic Electric Switch." By W. R. Wynne.

"Note on the Theory of Terrestrial Magnetism." By Profs. Ayrton and Perry.

February 28th, 1880.

Prof. W. G. Adams, M.A., F.R.S., Vice-President, in the Chair.

The following presents were announced:—

Bemerkungen über das Mechanische Æquivalent der Wärme. By J. R. Mayer. Presented by Prof. S. P. Thompson.

The following papers, by Dr. SCHUSTER, F.R.S. Presented by the Author:—

"On Unilateral Conductivity."

"On the Polarization of the Solar Corona."

"Experiments on Electrical Vibrations."

"On the Spectra of Metalloids (Oxygen)."

"Report of Total Solar Eclipse, April 6, 1875."

Ueber die Bestimmung der Brechungsenponenten mit totaler Reflexion. By Prof. QUINCKE. Presented by Dr. SCHUSTER.

The following papers were read:—

"On some Effects of Vibratory Motion in Fluids." By R. H. RIDOUT.

"On the Pneumatic Experiment of Clement Desormes." By R. H. RIDOUT.

"On the Determination of Chemical Affinity in terms of Electromotive Force." By Dr. C. R. ALDER WRIGHT.

March 13th, 1880.

Dr. HUGGINS, D.C.L., F.R.S., Vice-President, in the Chair.

The following were elected Members of the Society:—

Prof. G. M. MINCHIN, M.A.; JAMES HULME; AUGUSTUS STROH; Prof. D. E. HUGHES; Lieut. G. T. WINGFIELD, R.N.; J. MACFARLANE GRAY.

The following papers were read:—

"On the Surfusion of certain Metals." By W. C. ROBERTS.

"On a Novel Source of Electricity." By Prof. W. F. BARRETT.

"On the Influence of Friction upon the Generation of a Voltaic Current." By SHELFORD BIDWELL.

"Note on the Excitement of Electricity by the Friction of Non-conductors." By Prof. F. GUTHRIE.

"On the Efflux of a Liquid from an Expanded Pipe." By R. H. RIDOUT.

April 10th, 1880.

Prof. FULLER, M.A., in the Chair.

The following were elected Members of the Society:—

Prof. J. W. JUDD, F.R.S.; W. O. SMITH.

The following papers were read:—

"On the Human Eye as an Automatic Photometer." By W. ACKROYD.

"On Prof. Guthrie's Experiment relating to the Excitement of Electricity by the Friction of Non-conductors." By Profs. AYRTON and PERRY.

"On Kœnig's Tuning-fork Clock." By Dr. W. H. STONE.

Dr. GUTHRIE exhibited an experiment indicating the magnetic behaviour of a *magnetic* iron cylinder rotating in front of a conductor carrying a current parallel to its axis.

April 24th, 1880.

Prof. W. G. ADAMS, M.A., F.R.S., Vice-President, in the Chair.

The following present was announced:—

Saunier's Treatise on Horology. Presented by Mr. EDWARD RIGG.

The following were elected Members of the Society:—

THE MARQUIS OF BLANDFORD; JOHN MARSHALL, F.R.A.S.

The following papers were read:—

"Preliminary Note on Mr. Hall's recent Discovery of the Displacement of the Current in a Conductor of Magnetic Force." By Prof. H. A. ROWLAND.

"On a Correction to be applied to the Indications of the Bifilar Magnetometer, and also a new Method for the Absolute Measurement of the Horizontal Intensity." By H. WILD.

"On new Thermoelectric Apparatus." By R. H. RIDOUT.

Mr. RIDOUT also exhibited Apparatus for showing electrolysis, for measuring cohesion in liquids, for showing absorption of heat on liquifaction, and for showing production of musical notes in a continuous tube.

Dr. W. H. STONE exhibited photographs of Kœnig's Tonometer.

Prof. G. M. MINCHIN described some experiments he had recently made on photo-telegraphy.

May 8th, 1880.

Sir WILLIAM THOMSON, LL.D., F.R.S., President, in the Chair.

The following were elected Members of the Society:—

E. F. BAMBER, C.E.; Dr. EUGEN OBACH; Prof. H. E. ROSCOE, F.R.S.; R. D. TURNER, F.G.S.; HENRY WATTS, F.R.S.; EDWARD WOODS, C.E.

The following papers were read:—

"On Photo-Electricity." By Prof. G. M. MINCHIN.

"A new Form of Electrometer-key." By Dr. O. J. LODGE.

"On the Elimination of Air from Water." By Sir WILLIAM THOMSON.

"On Steam-Pressure Thermometers. By Sir WILLIAM THOMSON.

"On the Radiation of Water-Steam Pressure Thermometers." By Sir WILLIAM THOMSON.

May 22nd, 1880.

At the Cavendish Laboratory, Cambridge.

LORD RAYLEIGH, F.R.S., Vice-President, in the Chair.

Mr. W. N. SHAW exhibited an apparatus for distilling mercury at low temperatures.

Mr. SEDLEY TAYLOR exhibited an adaptation by Kœnig of an arrangement of Sir John Herschel's for studying the interference of sound; also an improvement on Powell's wave-apparatus.

Mr. POYNTING described an arrangement for measuring the plane of polarization of light.

Mr. GLAZEBROOK showed a different apparatus for the same purpose.

LORD RAYLEIGH gave an account of some observations he had made relating to the theory of colour.

The Members afterwards visited the various departments of the Cavendish Laboratory.

June 12th, 1880.

Dr. HUGGINS, F.R.S., Vice-President, in the Chair.

The following were elected Members of the Society:—

C. V. BOYS; ADAM HILGER; H. B. JUPP, F.R.S.

The following papers were read:—

"On the Earth's Rotation as influenced by Solar Energy." By Dr. SHETTLE.

"On the use of Interference-Bands for obtaining Indications of the Pressure of a Gas, and on the Passage of Electricity through Gaseous Media." By Prof. E. WIEDEMANN.

"On a Simple Method of Amplifying small Vibrations." By R. H. RIDOUT.

"On the Radiograph." By D. WINSTANLEY.

"On the Mathematical Explanation of the Figures of the Phoneidoscope." By WALTER BAILY.

June 26th, 1880.

Prof. W. G. ADAMS, M.A., F.R.S., Vice-President, in the Chair.

The following papers were read:—

"On Magneto-Electric Induction (Resistance of Liquids)." By F. GUTHRIE and C. V. BOYS.

"On the Refraction-equivalents of Isomeric Bodies." By Dr. J. H. GLADSTONE.

"On a Fire-damp Indicator." By Mr. LIVEING.

"Vacuum-tube of varying Resistance." By Dr. W. H. STONE.

"On Specific Heats calculated from Entropy." By J. MACFARLANE GRAY.

"On the Behaviour of Liquids and Gases near their Critical Temperatures." By J. W. CLARK.

"On some Varieties of Air-thermometer and a Thermograph." By D. WINSTANLEY.

"On a Modification of Bunsen's Ice-Calorimeter." By W. W. GEE and W. STROUD.

Dr. W. HUGGINS exhibited Photographs of Star Spectra and a Photograph of the Spectrum of Water.

November 13th, 1880.

Prof. W. G. ADAMS, M.A., F.R.S., Vice-President, in the Chair.

The following papers were read:—

"On the Beats of Mistuned Consonances of the form $h : 1$." By R. H. M. BOSANQUET.

"On Action at a Distance." By W. R. BROWNE.

"On the Thermodynamic Relations of the Thermal and Ergonal Constituents of Heat in Liquids, Vapours, and Gases." By J. MACFARLANE GRAY.

"On Professor Exner's papers on Contact Electricity and Polarization." By Profs. AYRTON and PERRY.

Prof. MINCHIN exhibited a Photoelectric cell.

November 27th, 1880.

Prof. W. G. ADAMS, M.A., F.R.S., Vice-President, in the Chair.

The following was elected a Member of the Society:—

H. CHAPMAN JONES, F.C.S.

The following papers were read:—

"On the Photophone." By Prof. A. GRAHAM BELL.

"On a Modification of Prof. Graham Bell's Photophone." By SHELFORD BIDWELL.

"On Refraction-equivalents." By Dr. J. H. GLADSTONE.

December 11th, 1880.

Prof. W. G. ADAMS, M.A., F.R.S., Vice-President, in the Chair.

The following were elected Members of the Society:—

WALTER RALEIGH BROWNE, M.A.; T. WRIGHTSON, C.E.

The following papers were read:—

"On the Rate of Decrease of Light from Phosphorescent Surfaces." By Lieut. DARWIN, R.E.

"On the Determination of Chemical Affinity in terms of Electromotive Force." By Dr. C. R. ALDER WRIGHT.

January 22nd, 1881.

Dr. GUTHRIE, F.R.S., and afterwards Prof. W. G. ADAMS, F.R.S., Vice-President, in the Chair.

The following was elected a Member of the Society:—

G. P. SIMPSON.

The following papers were read:—

"On the Construction of the Photophone." By Prof. S. P. THOMPSON.

"On a Method of measuring Small Resistances." By R. T. GLAZEBROOK.

"On a Method of comparing the Capacities of two Condensers." By R. T. GLAZEBROOK.

Annual General Meeting.

February 12th, 1881.

Prof. Sir WILLIAM THOMSON, LL.D., D.C.L., F.R.S., President, in the Chair.

The following Report of the Council was then read by the President:—

If in the past year the history of the Society has been uneventful, the objects in view when it was formed have been steadily pursued.

The number of Members has risen from 298 at the last Annual General Meeting to 321 at the present time. Fifteen Members have compounded during the past year, and three have resigned. The number of papers read shows a slight increase, and their interest and value has been well sustained.

With regard to publications other than the 'Proceedings,' it may be mentioned that the Council have had considerable difficulty in obtaining the services of a translator possessing both scientific knowledge and a thorough acquaintance with the Italian language,

and in consequence some delay has occurred in translating Volta's work. Progress is, however, now being made; and additional help in the work of translation is being obtained.

The delay is perhaps of less importance, as the Council has decided to undertake the publication of a complete edition of Mr. Joule's scientific papers. In this they have not only the assent but the warm and active cooperation of this distinguished Physicist, who has voluntarily taken upon himself the collection of his papers.

Early in the year the Society of Arts requested the Council to nominate a recipient for the Albert Medal, which is awarded annually for "distinguished merit in promoting Arts, Manufactures, or Commerce." After careful consideration, the Council unanimously determined that Dr. Joule's name should be submitted to the Society of Arts as well deserving the honour; and the Council is gratified to find that the suggestion was adopted, the grounds for the award being stated as follows:—"For having established, after most laborious research, the true relation between heat, electricity, and mechanical work, thus affording the engineer a sure guide in the application of science to industrial pursuits."

The Library has continued to receive valuable contributions, both from learned Societies at home and abroad, in the form of their 'Transactions' and 'Proceedings,' and from private individuals. One of the most interesting of the latter class is a volume of Minutes of a Society kindred to ours, which appears to have existed about the years 1794–95*. This volume, presented to the Society by Mr. Latimer Clark, contains evidence of the great intellectual activity at that time; and some of the experiments referred to are identical with some of those of our own day, although, of course, differently interpreted.

Your Library Committee will shortly seek for a grant out of the Society's funds for the purpose of completing and binding certain periodicals and pamphlets. The Committee would also urge upon the Members of the Society that, as the Library is still small, serious efforts should shortly be made for its proper organization and development, so that it may keep pace with the growth of the Society.

A Meeting of more than ordinary interest was held on the 22nd

* "The Minutes of the Society for Philosophic Experiments and Conversations." T. Cadell and W. Davies, Strand, 1795.'

of May at Cambridge, in the Cavendish Laboratory, by the invitation of Lord Rayleigh, and the Meeting was rendered specially pleasant by the kindness of the Master and Senior Fellows of St. John's College, who placed their library and combination rooms at the disposal of the Society.

With regard to the Funds of the Society, the Council, in October last, sought the legal advice of one of our Members, Mr. Frank Crisp, who wrote as follows:—"No provision is made in the Bye-Laws for investments, and the Council are therefore in the same position as Trustees in whose trust-deed nothing is said as regards investments." The Council has therefore no legal power to invest in such profitable sources of income as Railway Debentures or Preference Stock, and, in order that the necessary authority may be obtained, Mr. Crisp has kindly prepared the resolution that will be submitted to you to-day.

The Council is satisfied that the Society has been grateful to the Vice-Presidents, on whom, in the absence of our distinguished President, more than an ordinary share of duty has fallen.

The Society has to regret the loss of two Members by death. On the 8th of February, 1880, Sir Thomas Frederick Eliot died at Cairo, from typhoid fever. He was the son of the Rt. Hon. Hugh Eliot, sometime Governor of Madras. He was born in London in 1808, and was educated at Harrow. In 1825 he entered the Colonial Office, and was Secretary to the Earl of Gosford's Commission in Canada from 1835 to 1837, when he was appointed Chief of the first Department of Emigration in this country, an office which he held until 1847. From that date to the end of 1868 he held the post of Assistant Under Secretary of State for the Colonies, and he was nominated a Knight Commander of the Order of St. Michael and St. George in 1869. He was twice married, and survived his second wife but a few days. He joined this Society in 1879, and by his death we lose a distinguished Member of high official rank, who always had the advancement of science at heart.

The Rev. Arthur Rigg, M.A., who died on the 2nd September, 1880, at the age of 68, will long be remembered as one of the early pioneers in the cause of Technical Education. He was born on the 10th of March, 1812, at Carlisle, and received his early education at Warrington and in the Isle of Man. Matriculating at Christ's College, Cambridge, in 1832, he graduated in 1835 as 27th Wrangler, was immediately afterwards ordained, and was appointed Senior Mathematical and Philosophical Master at the Royal Insti-

tution in Liverpool. About this time there was much interest taken throughout the country in the question of training teachers for Church of England schools, and a highly influential meeting was held at Newton, near Warrington, on the 25th January, 1839, at which the details of a diocesan system of education were arranged, and it was resolved to build a large training college at Chester. Mr. Rigg was appointed its first Principal, and the College was opened in 1842, arranged to accommodate "50 training masters and 70 commercial scholars, together with all the officers of the establishment; and also 110 daily scholars in the modern school:" this latter was specially provided in order to afford the training masters actual practice in the teaching of such pupils as would subsequently be placed under their charge. From the first the advisability of combining with a sound intellectual education, instruction in the various manual trades was kept steadily in view. Besides the ordinary subjects taught in schools, the system of education comprised book-keeping, surveying, engineering, natural philosophy, and linear drawing; and the pupils, besides laboratory practice, were familiarized with the details of operative work; and in the workshops of the place they enjoyed an opportunity of becoming acquainted with the use of tools, the construction of machinery, the application of steam, principles of mechanics, statics, &c. In 1860 the school was certified as possessing all the requisites for the preparation of candidates for the Engineering Department of Public Works in India, and in the course of the next few years a considerable number went out to India in that service. Mr. Rigg resigned the Principalship in 1869, when nearly all of those who commenced the work with him had either died or left the diocese. He was a life member of the Society of Arts, a member of the Board of Visitors of the Royal Institution, a past member of the Institution of Mechanical Engineers, and an original member of our Society.

The Council would again call attention to the obligation under which the Society rests to the Lords of Committee of Council on Education for the use of the Physical Lecture Room and Laboratories so generously placed at its disposal; and they would also thank Dr. Guthrie, to whom the success of the Society is so largely due, for his important services as Demonstrator.

The Society then proceeded to the election of Council and Officers for the ensuing year; and the following gentlemen were declared duly elected:—

President.—Sir Wm. Thomson, LL.D., F.R.S.

Vice-President (who has filled the Office of President).—Prof. W. G. Adams, M.A., F.R.S.

Vice-Presidents.—Prof. R. B. Clifton, M.A., F.R.S.; Prof. F. Fuller, M.A.; W. Huggins, D.C.L., F.R.S.; Lord Rayleigh, M.A., F.R.S.

Secretaries.—Prof. A. W. Reinold, M.A.; Prof. W. Chandler Roberts, F.R.S.

Treasurer.—Dr. E. Atkinson.

Demonstrator.—Prof. F. Guthrie, Ph.D., F.R.S.

Other Members of Council.—Prof. W. E. Ayrton; Walter Baily, M.A.; Prof. J. H. Cotterill, M.A., F.R.S.; Prof. G. C. Foster, F.R.S.; J. Hopkinson, M.A., D.Sc., F.R.S.; R. J. Lecky, F.R.A.S.; Hugo Müller, Ph.D., F.R.S.; Prof. Osborne Reynolds, M.A., F.R.S.; Prof. A. W. Rücker, M.A.; A. Schuster, Ph.D., F.R.S.

The following were elected Honorary Members:—

John William Draper; Gustav Wiedemann.

After the names of the Council and Officers had been announced from the Chair, votes of thanks were passed:—to the Lords of the Committee of Council on Education; to the President; to Prof. Guthrie for his valuable services to the Society; to the Officers; and to the Auditors.

PROPERTY ACCOUNT OF THE PHYSICAL SOCIETY.

Assets.	£	s.	d.
Subscriptions due	40	0	0
£400 4 per cent. Debenture Stock Furness Railway at 103	412	0	0
£460 5 per cent. Midland Railway Preference Stock at 123	565	0	0
£200 Metropolitan Board of Works Stock	210	0	0
Due by Treasurer	13	17	6
Balance in Bank	167	13	10
	£1408	11	4

Liabilities.	£	s.	d.
Cheque unpaid	4	0	0
Subscriptions in advance	6	0	0
Balance	1398	11	4
	£1408	11	4

We have examined the above Account, and also the Securities at the Bank, and find the same to be correct.

London, February 2nd, 1881.

SHELFORD BIDWELL,
WALTER H. COFFIN, } *Auditors.*





